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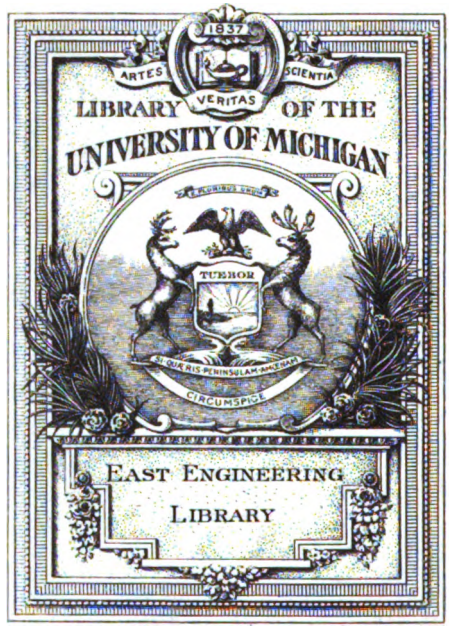
Transactions of the American Electrochemical Society

American Electrochemical Society



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TRANSACTIONS

OF THE

AMERICAN

ELECTROCHEMICAL SOCIETY.

VOLUME III.

THIRD GENERAL MEETING.
NEW YORK CITY, APRIL 16, 17, 18, 1903.

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY,
929 CHESTNUT ST., PHILADELPHIA, PA.
1903.

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Terms expire 1906.

TREASURER:

PEDRO G. SALOM, 408 Bourse Building, Philadelphia, Pa.
Term expires 1904.

SECRETARY:

CHAS. J. REED, 929 Chestnut St., Philadelphia, Pa.
Term expires 1904.

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VOLUME III. 1903.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS.

CONDENSED MINUTES OF THE THIRD GENERAL MEETING OF THE SOCIETY, HELD AT NEW YORK CITY, APRIL 16-18, 1903.

(Number of members registered, 122; guests, 138; total, 260.)

SESSIONS OF APRIL 16TH.

The meeting was called to order at 10 A.M., in the Assembly Hall of the Chemists' Club, by Vice-President Doremus, chairman of the Local Committee, who greeted the Society on behalf of the Local Committee, and called President Richards to the chair. The chairman gave the floor to Mr. Wm. McMurtrie, president of the Chemists' Club, who extended a warm welcome to the Society, stating that the Chemists' Club had not only placed the Assembly Hall at the disposal of the Society for holding its meeting, but that the rest of the club house, including the library of the American Chemical Society, was open to the visitors to use as their own while attending the meeting. The chair thanked Mr. McMurtrie for his words of welcome, and assured him of the Society's high appreciation of the courtesy of the Chemists' Club.

The reading of the minutes of the Second General Meeting of

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the Society, not being called for, was dispensed with, they having been printed in Vol. II of the Transactions.

The Secretary read an abstract of his annual report to the Board of Directors, which is printed in full in the proceedings of the Board (p. 7). The report showed the present membership to be 494.

The Treasurer read an abstract of his annual report to the Board of Directors, printed in full (p. 9). The report showed the Society to have ended the fiscal year, on December 31, 1902, with an excess of assets above liabilities of $592, and with 945 copies of the Transactions on hand, valued at two thousand dollars.

Papers by Prof. W. D. Bancroft, of Cornell University, Dr. H. T. Barnes, of McGill University (read by Prof. W. D. Bancroft), Dr. Jos. W. Richards, and W. S. Landis, of Lehigh University (read by Dr. Richards), Prof. W. D. Bancroft, and Mr. C. J. Reed, of Philadelphia, were then read and discussed, as published in full in the Transactions.

After luncheon served at the Chemists' Club by invitation of the New York members, the session was resumed at 2 P.M., and papers by Dr. M. von Recklinghausen, of New York, H. B. Coho, of New York, E. A. Sperry, of Cleveland, Ohio, Dr. W. H. Walker, of Boston, Mass., Dr. H. S. Carhart, of Ann Arbor, Mich., and A. A. Knudson, of New York, were read and discussed, as published in full in the Transactions.

At 7 P.M., the officers of the Society and the chairmen of the Local Committees held a reception in the club house parlors of the German Liederkranz, which club had also opened its house to members and guests of the Society during all the days of the meeting.

At 8 P.M., 121 members and guests sat down to a subscription banquet in the banquet hall of the German Liederkranz. There were present, as invited guests, Dr. Walter Nernst, of Göttingen, Germany, Chas. F. Scott, Esq., president of the American Institute of Electrical Engineers, Dr. A. R. Ledoux, president of the American Institute of Mining Engineers, Dr. Samuel Sheldon, president of the New York Electrical Society, Dr. Charles F. Chandler, of Columbia University, Dr. H. W. Wiley, chief of Bureau of Chemistry, Department of Agriculture, Wm. McMur-

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trie, Esq., president of the Chemists' Club of New York City, F. A. Ringler, Esq., president of the German Liederkranz, and Dr Joseph W. Richards, president of the American Electrochemical Society. Vice-president Chas. A. Doremus, of this Society, acted as toast-master, and responses were made by Dr. Richards, Professor Nernst, Chas. F. Scott, Professor Chandler, and Dr. H. W. Wiley.

SESSIONS OF APRIL 17TH.

The meeting was called to order at 9.30 A.M., in the Assembly Hall of the Chemists' Club.

The tellers of the annual election reported the result of their canvas of the voting for president, three vice-presidents, three managers, secretary and treasurer, as follows:

For President: (217 votes cast.) Dr. J. W. Richards, 160; A. H. Cowles, 35; E. G. Acheson, 9; W. D. Bancroft, 5; C. S. Bradley, 3; C. A. Doremus, 2; E. C. Klipstein, C. O. Mailloux, C. J. Reed, 1 each.

For Vice-Presidents: (636 single votes cast.) Prof. W. D. Bancroft, 147; Prof. C. A. Doremus, 145; Dr. W. R. Whitney, 119; A. H. Cowles, 50; C. E. Acker, 27; Carl Hering, 19; E. G. Acheson, 18; C. F. Burgess, 17; C. S. Bradley, 11; C. P. Steinmetz, 10; R. H. Thompson, 9; E. R. Taylor, 7; C. O. Mailloux, 5; F. J. Tone, D. H. Browne, S. Sheldon, W. H. Wahl, S. Reber, 4 each; N. S. Keith, E. A. Byrnes, J. W. Richards, C. J. Reed, 3 each; T. Ulke, G. G. Pond, H. T. Barnes, A. von Isakovics, H. S. Carhart, A. W. Smith, 2 each; A. E. Kennelly, J. D. Darling, J. W. Langley, E. F. Roeber, S. P. Sadtler, H. N. Potter, W. McA. Johnson, Townsend Wolcott, 1 each.

For Managers: (633 single votes cast.) Col. S. Reber, 150; Dr. S. P. Sadtler, 137; C. O. Mailloux, 134; C. F. Burgess, 20; C. E. Acker, 18; C. P. Townsend, 16; F. B. Crocker, 15; W. D. Bancroft, 13; J. W. Richards, 11; C. A. Doremus, T. Wolcott, F. J. Tone, 10; A. H. Cowles, 8; W. R. Whitney, 7; C. J. Reed, 6; D. H. Browne, E. A. Byrnes, C. S. Collins, N. S. Keith, E. R. Taylor, 5 each; J. D. Darling, W. E. Case, 4 each; H. T. Barnes, 3; E. J. Houston, H. B. Coho, C. S. Bradley, R. M. Thompson, C. P. Poole, E. H. Mullin, H. G. Morris, 2 each; H. N. Potter, J. L. R.

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Morgan, J. S. C. Wells, M. von Recklinghausen, A. W. Smith, H. S. Carhart, E. A. Sperry, C. F. Mabery, Carl Hering, N. Dodge, W. M. Johnson, S. Sheldon, E. N. Dickerson, E. G. Acheson, 1 each.

For Treasurer: (211 votes cast.) Pedro G. Salom, 204; W. McA. Johnson, 4; E. F. Roeber, 2; A. von Isakovics, 1.

For Secretary: (214 votes cast.) Charles J. Reed, 210; P. G. Salom, Carl Hering, S. P. Sadtler, E. F. Roeber, 1 each.

Total number of envelopes received from the Secretary, 235, of which 11 were rejected for non-payment of dues and 6 were unidentified, leaving 218 ballots to be counted.

We find that J. W. Richards is elected president; W. D. Bancroft, C. A. Doremus and W. R. Whitney are elected vice-presidents; S. Reber, S. P. Sadtler and C. O. Mailloux are elected managers; P. G. Salom, treasurer; C. J. Reed, secretary.

G. W. PATTERSON,
C. F. BURGESS,
Tellers.

On motion, the report of the tellers was adopted, and the tellers thanked for their arduous services.

Papers by Dr. N. S. Keith, of New York, Titus Ulke (read by Dr. Jos. W. Richards), Dr. W. Nernst, of Göttingen, Germany, Prof. W. D. Bancroft, of Cornell University, Dr. Louis A. Parsons, of Johns Hopkins University, Carl Hering, of Philadelphia, Prof. W. D. Bancroft, Prof. C. F. Burgess and Dr. Carl Hambuechen, of the University of Wisconsin (read by Prof. Burgess), were then read and discussed, as printed in full in the Transactions.

After luncheon, served at the Chemists' Club by invitation of the New York members, the afternoon was spent in visits to industrial establishments and other points of interest.

At 8 P.M. the Society was, by special invitation, the guest of the American Institute of Electrical Engineers at their extra meeting, held in the chapel of the College of the City of New York, at which Mr. Wm. J. Hammer delivered a lecture, illustrated by numerous experiments, on "Radium and Other Radioactive Substances, and Certain Phosphorescent and Fluorescent Substances. The Properties and Applications of Selenium. The Treatment of Disease by

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Ultra-Violet Rays." By the courtesy of the American Institute of Electrical Engineers, Mr. Hammer's lecture is printed as an *Appendix* to this volume of Transactions.

SESSIONS OF APRIL 18TH.

The meeting was called to order at 9.30 A.M., in the Assembly Hall of the Chemists' Club, President Richards in the chair.

Papers by J. G. Zimmerman, of the University of Wisconsin (read by Prof. C. F. Burgess), A. B. Marvin, of the U. S. Patent Office, Washington, Dr. H. E. Patten, and W. R. Mott, of the University of Wisconsin (read by Mr. Mott), W. McA. Johnson, of New Haven, Conn., Barry MacNutt, of Lehigh University, and Jos. A. Steinmetz, of Philadelphia (read by Jos. W. Richards), were read and discussed, as printed in full in the Transactions.

Mr. A. Eimer, of the firm of Eimer & Amend, New York City, exhibited a collection of the most recent forms of laboratory electric furnaces, and their products. Papers by J. W. Walker, Ph.D., C. W. Volney and W. R. Whitney were read by title, and are printed in full in the Transactions.

After luncheon, served at the Chemists' Club by invitation of the New York members, the afternoon was spent in visits to industrial establishments and other points of interest.

At 8 P.M. the meeting was resumed in the Assembly Hall of the Chemists' Club, where, before an audience of nearly 400 members and guests, President Richards delivered the *Presidential Address,* on the subject "Conditions of Progress in Electrochemistry,"—as printed in full in the Transactions.

At the close of the address (which was received with prolonged applause) Prof. W. D. Bancroft moved that the thanks of the Society be extended to the Chemists' Club of New York City, to the German Liederkranz, to the officials of the Brooklyn Navy Yard, to Messrs. Eimer & Amend, the Crocher-Wheeler Electric Co., Sawyer-Mann Electric Co., Willyoung & Gibson Co., the officials of the power houses visited, and to the New York members of the Society, particularly to their Local Committees.

Mr. P. H. Thomas exhibited the Cooper-Hewitt Vapor Converter in operation, and explained by diagrams the principle on which it works. Dr. Max von Recklinghausen showed the Cooper-Hewitt Mercury-Vapor Electric Lamp, and demonstrated its actinic properties by photographs.

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The rest of the evening was passed in the social function designated on the program as a German-American Smoker (Kneipe), which was thoroughly enjoyed by all present.

C. J. REED,
Secretary.

BOARD OF DIRECTORS.

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF THE BOARD OF DIRECTORS AND ITS EXECUTIVE COMMITTEE,

OCTOBER, 1902—APRIL, 1903.

The Board has held stated monthly meetings, and the Executive Committee several additional ones, in the above interval, at which the following action was taken on matters of interest to the Society at large:

Regular meetings of the Executive Committee of the Board of Directors are held on the first Saturday of each month, at the office of the Society, 929 Chestnut Street, Philadelphia, at 2.30 P.M.

Reprints of papers, with discussion thereon, published by the Society, will be furnished free to the author, to the number of 50 copies, with covers, with the original paging. Additional reprints may be ordered by the authors at their own expense from the printers of the Transactions.

The Publication Committee shall, at its option, omit from the printed Transactions all papers and portions of papers read at the meetings, and all discussions thereon, which do not relate to the subject of electrochemistry.

The Secretary was authorized to exchange Vol. I in cloth for paper-bound copies returned in good condition by members, on payment of an additional sum of twenty-five cents.

The Secretary was instructed to procure an official seal with which to stamp all formal official communications from the Society.

At the meeting of the Board of Directors in New York City, April 16th, at which eleven of the eighteen members of the Board were present the Secretary reported on the condition of the Society as follows:

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SECRETARY'S ANNUAL REPORT.

April 3, 1902-April 16, 1903.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN—I submit herewith the following report on the condition of the Society, as required by your By-Laws.

The Society was organized at Philadelphia, April 3, 1902, and has held two general meetings, the Inaugural Meeting and a meeting at Niagara Falls, September 15-18, 1902.

The Transactions have been published in two volumes, including forty-one papers and the discussions thereon.

Of the 1,000 copies of each volume printed we still have on hand:

Number of copies of Vol. I in paper	48
Number of copies of Vol. I in cloth	276
Number of copies of Vol. II in cloth	543
Total	867

The following data show the condition of the Society in regard to membership:

Total number of applications considered to April 16, 1903		522
Resigned	6	
Reinstated after resignation	1	
	— 5	
Applications withdrawn	4	
Deceased	5	
Failed to qualify:		
Election of April 3, 1902	13	
Election of October 2, 1902	3	
	—16	
Total deductions		30
Present membership		492
Number of volunteers to charter membership		353
Number of applications since passed upon		166
Number of foreign members		53
Number of foreign countries represented		11
Number of states and territories in the United States represented		36

The Secretary would recommend that some systematic method of increasing our membership be put into operation. There are undoubtedly very many who are entirely ignorant of the existence

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of the Society who would be desirable members and glad to join, if information concerning the Society were placed before them.

It may be too early at the present time to do anything towards the establishment of local branch organizations, but at the present rate of increase of the Society it is evident that the organization of local branches in the near future will be desirable, if not a necessity. The past year has witnessed the inauguration of this plan by the American Institute of Electrical Engineers and the result has been a marked success even in the short time that it has been in operation. There seems to be no doubt that local branch organizations in the large cities would be able to contribute materially to the value of our published Transactions.

The organization of the Faraday Society in England, with 190 charter members, following within a few months of our own organization, is additional evidence, if any is needed, that the organization of an electrochemical society in the United States was entirely justified.

It would seem to be desirable and to the interest of all members if our Society could cooperate in some way with European electrochemical societies. A general method which I would suggest would be that equitable arrangements be made with such societies to supply our members residing in this country with their Transactions at a reduced rate. In exchange we could supply their members with our Transactions at a reduced rate. Such a plan would give a wider circulation to the Transactions of all of the societies.

In accordance with instructions of the Board of Directors I have placed an insurance of $1,500 on the copies of our Transactions now on hand.

Very respectfully submitted,

C. J. REED,
Secretary.

The Treasurer then reported on the state of the finances of the Society as follows:

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TREASURER'S ANNUAL REPORT.

Year ending December 31, 1902.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN—Herewith I beg to submit my report and condensed balance sheet, as treasurer of the American Electrochemical Society for the year ending December 31, 1902.

	Abstract of trial balance.		Loss.	Gain.	Assets.	Liabilities.
Cash	879.49				879.49	
Annual dues		2205.00		2205.00		
Entrance fees		445.00		445.00		
Advertising account		339.84		339.84		
Publication account	1340.55		1340.55			
Expense	1057.50		1057.50			
Accounts collectable	163.70				163.70	
Accounts payable		676.80				676.80
Dues from members	255.40				255.40	
Dues, 1903, prepaid		30.00				30.00
	3696.64	3696.64	2398.05	2989.84		
Balance gain			591.79			
			2989.84	2989.84	1298.59	706.80
Balance present worth						591.79
					1298.59	1298.59

Receipts:

From 333 charter members		$1664.90
Entrance fees from 74 new members		370.00
Annual dues from 74 new members		364.70
From publications		121.70
From expense account		13.67
From advertising		222.50
Dues for 1903, prepaid		30.00

Expenditures:

Expenses	$1059.67	
Publication account	816.27	
Advertising account	32.04	
Balance in 4th St. National Bank	879.49	
	$2787.47	$2787.47
The cash in bank December 31st, 1902, was		879.49
Of this balance there was due from publication and expense incurred during the year	676.80	
Also 1903 account, for dues prepaid	30.00	
		706.80
Leaving a balance after all liabilities are paid		$ 172.69

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Total brought forward from preceding page		$ 172.69
Other assets are :		
Amounts due from members		255.40
Amount due for advertising		163.70
Giving a gain for the year 1902, of		$ 591.79

providing all the accounts are paid.

Note: Some of the above charges are against members who will possibly not qualify.

I also append statement of the financial condition of the Society to date (April 16th).

Cash in bank, April 15, 1903		$2172.73
Cash due from 93 members at $5		465.00
Cash due from 19 members at $10		190.00
		$2827.73
Receipts :		
Cash balance January 1, 1903		879.49
Cash received from members (annual dues)	$1965.00	
Initiation fees	300.00	
		2265.00
Cash received from publication account		158.89
Cash received from advertisements		147.86
Expenditures. (Vouchers 42 to 58.)		
Expenses	$ 426.23	
Publication	817.78	
Office furniture	34.50	
Cash balance in bank	2172.73	
	$3451.24	$3451.24

We have examined all of the above accounts and vouchers, to December 31st, 1902, and find same correct.

SAMUEL P. SADTLER,
HENRY G. MORRIS,
Auditing Committee.

All of which is respectfully submitted,

PEDRO G. SALOM,
Treasurer.

Mr. A. B. Frenzel, of Denver, Col., being present by invitation of the Board, offered the sum of $250 as a prize to the member of this Society presenting the best paper embodying his research on *practical methods of treating the rare minerals found in America, and extracting the rare metals therefrom*, leaving the decision of the award of the prize to the governing board of this Society. He also offered to furnish, for research purposes, free on board cars at point of shipment, any reasonable quantity of such ores as were

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at his disposal, *viz.*, ores of uranium, vanadium, molybdenum and tungsten.

The proposition was accepted, and a vote of thanks extended to Mr. Frenzel for his generous offer.[1]

The following were then adopted as the By-Laws of this Society:

BY-LAWS.

1. *Order of Business.*—At the annual meeting of the Society the order of procedure of the business session shall be as follows:

Reading of the minutes of last meeting.

Report of the Board of Directors, including those of the Secretary and the Treasurer.

Report of Standing Committees.

Deferred business.

New business.

Report of tellers of election.

Address of the retiring president. (This may be deferred to a later session of the general meeting, at the discretion of the framers of the program of the meeting.)

The business meeting of the Society shall preferably be the second day of the annual meeting.

2. *Meetings of the Board of Directors.*—The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society, or at the annual meeting at any time before the business meeting of the Society.

Between said meetings the Board of Directors may hold special meetings when called by the president, and coincident with monthly meetings of the Executive Committee when applications for membership are to be acted upon.

At the regular meetings of the Board of Directors the order of procedure shall be as follows:

Reading of the minutes of the last regular meeting and of any special meeting, the minutes of which have not been approved.

Election of new members.

Appointment of tellers of election.

Approval of bills.

[1] The prize is now in the hands of the Treasurer of the Society, and is open to any member of the Society wishing to present work in this direction to the consideration of the Board of Directors.

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Communications from the secretary.
Communications from the treasurer.
Communications from the president.
Report of committees.
Deferred business.
New business.
Adjournment.

At special meetings of the Board of Directors, the order of procedure shall include the reading of the minutes of the last meeting of the Board and such other of the above items of procedure in their order given as are to be acted upon.

3. *Duties of Officers.*—The president shall preside at all meetings of the Society and at those of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors. The president (or any director) shall have the power of appealing any action of the Executive Committee to the Board of Directors, within two weeks of its adoption, which action can then be carried into effect only after approval by a majority of the entire Board of Directors voting on said explicit action either in person or by mail ballot. He shall deliver an address at the annual meeting of the Society at which his term of office expires.

The vice-presidents, in the order of their seniority, shall assume the duties and responsibilities of the president in case of his death, disability or absence from fulfilling his duties.

The secretary, besides performing the usual duties of that office, shall be the guardian of the records of the Society, collect dues from members and all bills owing to the Society, and pay such amounts to the treasurer. At meetings of the Society he shall collect and receive manuscripts of the papers read with drawings or diagrams thereto belonging and shall be responsible for their custody until he hands them to the Publication Committee. He shall report to the Board of Directors at its meeting held at the annual meeting of the Society, on the condition of the affairs of the Society, such as the membership, publications, number of meetings, number of papers read and in general a summary of the work and condition of the Society, excepting its finances, and make such recommendations as he thinks will facilitate the transactions of the business affairs of the Society or in any way advance its interests.

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The treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society and make such recommendations as will in his opinion tend to safeguard or improve the same.

The Board of Directors shall report to the annual meeting on the general affairs of the Society including the abstracts of the reports of the secretary and the treasurer and any other matters which they may consider of interest to the Society.

4. STANDING COMMITTEES.—*Publication Committee.*—A Publication Committeee, consisting of at least five members, shall be appointed annually by the incoming president and approved by the Board of Directors, and shall have charge of all publications for one year beginning with the transactions of the meeting following the annual meeting .

Committee on Papers.—A Committee on Papers, consisting of at least five members, shall be appointed annually by the incoming president and approved by the Board of Directors, and shall procure and pass upon all papers for the meeting for one year, beginning with the meeting following the annual meeting.

The Publication Committee shall receive from the Secretary the manuscripts of papers read before the Society with illustrations or diagrams pertaining thereto and the discussion thereon, and shall publish the transactions of the Society. It shall have power to decide on the fitness of such matters for publication and in consultation with the authors to edit such matter, so that its publication may serve the best interests of the Society. It may edit the discussion so as to give it proper literary and parliamentary form, but not, however, changing its substance and meaning without the consent of the author.

The president and secretary shall be members *ex-officio* of all Standing Committees.

5. *Annual Election.*—The Board of Directors at its meeting immediately preceding the business session, at the annual meeting of the Society, shall appoint three tellers and an alternate for each.

The polls shall close at 5 P.M. of the first day of the annual meeting, after which the Secretary shall deliver to the tellers all ballots received by him, marking the outside envelopes received from

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members not entitled to vote. The tellers shall open only the envelopes not thus marked. All ballots and unopened envelopes shall be returned to the Secretary, who shall preserve them for one month. At the end of one month the Secretary shall return to the senders all rejected envelopes and shall open all unidentified envelopes. Cumulative voting is not permitted. Cumulative votes shall count as one vote.

6. *Quorum of Directors.*—A quorum of the Board of Directors shall be twelve, present in person or by proxy.

7. *Treasurer's Accounts.*—The President shall appoint two auditors, at least one week before the annual meeting, to audit the accounts of the treasurer. At least one of the said auditors shall be a member of the Board of Directors, and said member shall report the result of said audit to the Board of Directors at its meeting, preceding the annual business meeting of the Society.

8. *Entrance Fees.*—Any entrance fee paid by an applicant shall be returned if the applicant is not elected.

9. *Guests at Meetings.*—Guests may be introduced to the meeting of the Society by members and may be given the privilege of attending the meetings and may be given such further privileges as may be extended to them by the Local Committee or the President or Secretary.

10. *Membership Committee.*—A committee on membership, where function shall be to enlarge by systematic effort the membership of the Society, shall be appointed annually by the incoming president. It shall consist of 15 or more members.

The following were elected to membership at the stated monthly meetings:

December 4, 1902.

Dr. L. Paget, New York; Prof. Dr. Julius Wagner, Leipzig, Germany; R. W. Vicarey, Stafford, England; Prof. Philippe A. Guye, Geneva, Switzerland; Leonard Wilson, Pittsfield, Mass.; Dr. Wm. Dreyfus, New York; C. J. Pretzfeld, Niagara Falls; August Eimer, New York; Dr. John Shields, London, England; Prof. D. McIntosh, Montreal, Can.; Dr. J. W. Walker, Montreal, Can.; W. S. Landis, Bethlehem, Pa.; G. P. Adamson, Easton,

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Pa.; Victor Engelhardt, Vienna, Austria; F. J. Machalske, Chicago, Ill.

January 8, 1903.

Theron C. Stearns, Jersey City, N. J.; Abraham Van Winkle, Newark, N. J.; Prof. C. F. Chandler, New York; Gustave Drobegg, New York; Prof. Alfred Stansfield, Montreal, Can.; Dr. Victor Goldschmidt, Heidelberg, Germany; Dr. H. W. Wiley, Washington, D. C.; Samuel B. Devlin, New York; Joseph Wetzler, New York; Walter M. Stein, Primos, Del. Co., Pa.; Dr. C. Kellner, Vienna, Austria; Dr. R. Hammerschmidt, Frankfort a/M, Germany.

February 5, 1903.

L. Seeger, New York; Dr. R. de Neufville, Frankfort a/M, Germany; Dr. Hans Landolt, Turgi, Switzerland; J. M. Morehead, Chicago; William Smith Horry, Niagara Falls; C. I. Zimmerman, Madison, Wis.; John W. Schlegel, New York; Craig R. Arnold, Sharon Hill, Pa.; August J. Rogers, Milwaukee, Wis.; O. M. Thowless, Newark, N. J.; G. L. Cabot, Boston, Mass.; Joseph B. Hall, Chicago, Ill.; Francis W. Higgins, Niagara Falls; R. S. Allyn, New York; Ralph McNeill, New York; Takakichi Nakayama, Kochi, Japan.

March 5, 1903.

Alexander S. Garfield, Paris, France; Louis S. Gates, Parral, Chih., Mexico; Lee Shepherd, Midland, Mich.; John L. Clawson, Philadelphia; F. J. Davis, Lockport, N. Y.; John J. Riker, New York; Wm. Roy Mott, Madison, Wis.; C. F. Carrier, Jr., Bethlehem, Pa.; H. M. Backus, Bayonne, N. J.; J. W. Aylsworth, East Orange, N. J.; E. N. Dickerson, Stovall, N. C.; Wm. Battle Phillips, Austin, Tex.; C. R. Walker, Cambridge, Mass.; Walter G. Graves, Cleveland, Ohio; Albert Finck, Cleveland, Ohio; Daniel R. Warmington, Cleveland, Ohio; Prof. C. F. Mabery, Cleveland, Ohio.

April 4, 1903.

J. Turner Morehead New York; Thomas A. Edison, Orange, N. J.; H. A. Skelton, Foyers, Scotland; George F. Seward, New York; Wm. B. Rankine, Niagara Falls; Van Rensselaer Lansingh, Chicago; Augustus E. Knorr, Baltimore, Md.; Richard Trelfall,

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Birmingham, England; Ottis E. Acker, Niagara Falls; Samuel Newton Smith, Minneapolis, Minn.; B. H. Hite, Morgantown, W. Va.; Edward F. Kern, Lansingburgh, N. Y.; C. H. Moritz, Niagara Falls, N. Y.; Walter A. Wood, Gramercy Park, New York: G. H. Benjamin, New York; Charles Baskerville, Chapel Hill, N. C.

April 16, 1903.

H. O. Havemeyer, Jr., New York; Edgar Park, New York; Alexander Dick, London, England; Francis C. McMillin, Cleveland, Ohio; Ervin S. Ferry, Lafayette, Ind.; Samuel F. Hall, Niagara Falls; Dr. J. E. Mills, Chapel Hill, N. C.; Dr. Virgil Coblentz, New York.

May 9, 1903.

J. J. Kennedy, New York; M. Temple Taylor, Savannah, Ga.; Archibald Meldrum, Savannah, Ga.; Charles D. Chasteney, New York; Howard W. DuBois, Philadelphia; Joseph P. Devine, Buffalo, N. Y.; J. S. Crider, Cleveland, Ohio; Herman Poole, New York; Clarence Everett Doolittle, Aspen, Colo.; S. Lawrence Bigelow, Ann Arbor, Mich.; Dr. Charles B. Dudley, Altoona, Pa.; Emanuel Stein, New York; William L. Nadolsky, New York; E. H. Whitlock, Cleveland, Ohio; Arthur Benjamin Frenzel, Denver, Colo.; Frank Warren Smith, Los Catos, Cal.; E. A. C. Smith, Baltimore, Md.; Hans A. Frasch, New York.

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AMERICAN ELECTROCHEMICAL SOCIETY.

CATALOGUE OF MEMBERS.

(May 9, 1903.)

*[Members of date April 3, 1902, are charter members.]

		Date of election.*
Acheson, E. G.	International Acheson Graphite Company, Niagara Falls, N. Y.	Apr. 3, 1902
Acker, Charles E.	Acker Process Company, Niagara Falls, N. Y.	Apr. 3, 1902
Acker, O. E.	Acker Process Company, Niagara Falls, N. Y.	Apr. 4, 1903
Adams, Prof. Comfort A.	Assistant Professor of Electrical Engineering, Harvard University, Res. 13 Farrar St., Cambridge, Mass.	Apr. 3, 1902
Adams, Ernest K.	455 Madison Ave., New York.	Apr. 3, 1902
Adams, Geoffrey C., C.E., M.A.	Chief Engineer, Columbian Carbide Company, Res. New Amsterdam Hotel, New York.	Apr. 3, 1902
Adams, Dr. Isaac	1776 Massachusetts Ave., Cambridge, Mass.	Apr. 3, 1902
Adamson, G. P.	General Manager, The Baker & Adamson Chemical Company, Res. 233 Reeder St., Easton, Pa.	Dec. 4, 1902
Addicks, Lawrence	Raritan Copper Works, Perth Amboy, N. J.	Apr. 3, 1902
Alden, John	Pacific Mills, Lawrence, Res. Andover, Mass.	Apr. 3, 1902
Allen, Wyatt H.	Consulting Engineer, 331 Pine St., San Francisco, Cal.	Sep. 4, 1902
Allyn, R.S.	Lawyer, 41 Park Row, Res. 174 W. 82nd St., New York.	Feb. 5, 1903
Amster, N. L.	Consulting Mining Engineer, 32 Equitable Building, Boston, Mass.	Apr. 3, 1902
Anderson, Edw. L.	Electrochemist, Anderson Electric Mfg. Company, 119 N. 11th St., St. Louis, Mo., Res. 2700 Euclid Ave., St. Louis.	July 3, 1902
Arden, Henry	900 Pine St., San Francisco, Cal.	Oct. 2, 1902
Arnold, Craig R.	Sharon Hill, Pa.	Feb. 5, 1903
Askew, C. B.	Consulting Engineer, 1652 Monadnock Building, Chicago, Ill.	Apr. 3, 1902

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		Date of election.*
Atwood, Geo. F.	Western Electric Company, New York.	Apr. 3, 1902
Austen, Peter T., Ph.D., F.C.S.	80 Broad St., New York.	Apr. 3, 1902
Aylsworth, J. W.	Chemical Engineer and Experimenter, Edison Storage Battery Company, Res. 223 Midland Ave., East Orange, N. J.	Mar. 5, 1903
Backus, H. M.	Chemist, Orford Copper Company, Res. 47 Avenue C, Bayonne, N. J.	Mar. 5, 1903
Bakewell, Thos. W.	Patent Lawyer, Carnegie Building, Pittsburg, Pa.	Apr. 3, 1902
Bancroft, Wilder D., Ph.D.	Cornell University, Ithaca, N. Y.	Apr. 3, 1902
Banks, Wm. C.	Gordon Battery Company, 439-445 E. 144th St., New York.	Apr. 3, 1902
Barker, E. R.	Burgess Sulphite Fibre Co., Berlin, N. H.	Apr. 3, 1902
Barnes, H. T., Ph.D.	McGill University, Montreal, Can.	Apr. 3, 1902
Barnes, S. G.	Electrical Engineer, Solvay Process Co., 310 Boulevard West, Detroit, Mich.	Apr. 3, 1902
Barr, B. M.	234 E. 21st St., Flatbush, L. I.	Apr. 3, 1902
Barstow, W. S.	Consulting Engineer, Bowling Green Offices, New York, Res. 868 Park Place, Brooklyn, N. Y.	Apr. 3, 1902
Bartol, H. W.	31, Bd. Victor Hugo, Nice, France.	Apr. 3, 1902
Barton, Chas. B.	Superintendent of Electrolytic Bleach Plant, Burgess Sulphite Fibre Co., Berlin, N. H.	Sep. 4, 1902
Baskerville, Chas., Ph.D.	Professor of Chemistry, Director of Laboratory, University of North Carolina, Chapel Hill, N. C.	Apr. 4, 1903
Batchelor, Chas.	52 Broadway, New York.	Apr. 3, 1902
Bates, Wm. S.	Consulting Engineer, 510 Boylston Building, Chicago, Ill.	Apr. 3, 1902
Becket, Fred. M.	170 Buffalo Ave., Niagara Falls, N. Y., Box 158.	Apr. 3, 1902
Behrend, Dr. O. F.	Erie, Pa.	Apr. 3, 1902
Benjamin, Dr. G. H.	45 Broadway, Res. 20 W. 11th St., New York.	Apr. 4, 1903

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		Date of election.
Benoliel, Sol. D., B.S., E.E., A.M.	General Manager Roberts Chemical Works, Res. 14 C St., Niagara Falls, N. Y.	Sep. 4, 1902
Berg, Ernst J.	Electrical Engineer, General Electric Company, Schenectady, N. Y.	Oct. 2, 1902
Betts, Anson G.	Care Earl & Wilson, Troy, N. Y.	Apr. 3, 1902
Bierbaum, C. H.	Lumen Bearing Co., 1155 Sycamore St., Res. 312 Prospect Ave., Buffalo, N. Y.	Apr. 3, 1902
Bigelow, S. Lawrence, Ph.D.	Assistant Professor of General Chemistry, University of Michigan, Res. 1520 Hill St., Ann Arbor, Mich.	May 9, 1903
Bishop, Walter B.	Assistant Assayer, Granby Smelting, Mining & Power Co., Grand Forks, B. C.	Sep. 4, 1902
Bixby, George L.	Assistant Treasurer and Superintendent The Willard Storage Battery Co., 49 Wood St., Cleveland, Ohio.	Aug. 7, 1902
Blackmore, Henry S.	206 S. 9th Ave., Mount Vernon, N. Y.	Apr. 3, 1902
Bleecker, John S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Block, Wesley S.	President Roberts Chemical Company, 40 Wall St., New York.	Oct. 2, 1902
Böttinger, Dr. H. T.	President of *Deutsche Bunsen Gesellschaft*, Berlin, Res. Elberfeld, Germany.	Sep. 4, 1902
Bogue, Chas. J.	Manufacturer of Electric Machinery, 213-215 Center St., New York	Apr. 3, 1902
Bolling, Randolph	Superintendent of the Victoria Furnace, Goshen, Va.	Apr. 3, 1902
Boon, Prof. John D.	School of Physics and Chemistry, John Tarleton College, Stephenville, Tex.	Apr. 3, 1902
Bostick, E. E., M.D.	American Synthetic Company, 3600 N. 5th St., Philadelphia, Pa.	Apr. 3, 1902
Bowman, Walker	39 Cortlandt St., New York.	Apr. 3, 1902
Boynton, Dr. C. S.	Burlington, Vt.	Apr. 3, 1902
Bradley, Chas. S.	President Atmospheric Products Co., 44 Broad St., New York.	Nov. 6, 1902
Bradley, Walter M.	Sheffield Scientific School, Chemical Laboratory, Res. 1346 Chapel St., New Haven, Conn.	Apr. 3, 1902

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		Date of election.*
Brill, Geo. M.	Consulting Engineer, 1134 Marquette Building, Res. 6510 Yale Ave., Chicago, Ill.	July 3, 1902
Brindley, Geo. F.	Niagara Electro-Chemical Co., Niagara Falls, N. Y.	Apr. 3, 1902
Brock, Robert C. H.	1612 Walnut St., Philadelphia, Pa.	Apr. 3, 1902
Brooks, Prof. Morgan	University of Illinois, Urbana, Ill.	Apr. 3, 1902
Brown, Harold P.	Electrical Engineer, 120 Liberty St., New York.	Apr. 3, 1902
Brown, J. Stanford	489 Fifth Ave., New York.	Apr. 3, 1902
Brown, Oliver W.	Instructor on Electrochemistry, Indiana University, Bloomington, Ind.	Apr. 3, 1902
Brown, W. G.,B.S., Ph.D.	Professor of Chemistry, University of Missouri, Columbia, Mo.	Apr. 3, 1902
Browne, David H.	Chief Chemist, Canadian Copper Company, Copper Cliff, Ont.	Apr. 3. 1902
Browne, William Hand, Jr.	Editor Electrical Review, Park Row Building, New York, Res. 431 Beech St., Richmond Hill, New York.	Apr. 3, 1902
Buchanan, Leonard B.	Stone & Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Burbank, Prof. J. E.	Instructor in Physics, University of Maine, Orono, Me.	Apr. 3, 1902
Burgess, Prof. C. F.	University of Wisconsin, Madison, Wis.	Apr. 3, 1902
Byrnes, Eugene A., Ph.D.	Patent Lawyer, 918 F Street, N. W., Res. 2539 13th St., Washington, D. C.	Apr. 3, 1902
Cabot, G. L.	82 Water St., Boston, Res. 16 Highland St., Cambridge, Mass.	Feb. 5, 1903
Caldwell, Edward	114 Liberty St., New York, Res. 50 Westervelt Ave., Plainfield, N. J.	Apr. 3, 1902
Cameron, Walter S.	239 W. 136th St., New York	Apr. 3, 1902
Capp, J. A.	Chief of Testing Laboratory, General Electric Company, Schenectady, N. Y.	Sep. 4, 1902
Carhart, H. S., LL.D.	University of Michigan, Ann Arbor, Mich.	Apr. 3, 1902
Carnaghan, E. D.	Villa Corono, Durango, Do., Ventanas, Consolidated Mining & Milling Co., Mexico.	Apr. 3, 1902
Carrier, C. F.	511 Union Place, Elmira, N. Y.	Mar. 5, 1903

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		Date of election.*
Carveth, Prof. Hector R.	Cornell University, Ithaca, N. Y.	Apr. 3, 1902
Case, Willard E.	Auburn, N. Y.	Oct. 2, 1902
Cates, Louis S.	National Steel and Wire Company, 18 Post Office Sq., Boston, Mass., and Parral, Chih., Mex.	Mar. 5, 1903
Chandler, Dr. C. F.	Professor of Chemistry, Columbia University, West 116th St., New York.	Jan. 8, 1903
Chasteney, C. D.	74 Cortlandt St., New York, Res. Rutherford, N. J.	May 9, 1903
Cheney, W. C.	Electrical Engineer, Park Place, Portland, Ore., Box 449.	Apr. 3, 1902
Chiaraviglio, Ing. Dino.	Société "Nobel," Avigliano (Farino), Italy.	Apr. 3, 1902
Childs, D. H.	New Kensington, Pa.	Apr. 3, 1902
Clamer, G. H.	Ajax Metal Co., Philadelphia, Pa.	Apr. 3, 1902
Clare, James P.	51 Edison St., Quincy, Mass.	Apr. 3, 1902
Clark, Friend E.	West Virginia University, Morgantown, W. Va.	Apr. 3, 1902
Clark, Wm. J.	The British Thomson-Houston Co., Ltd., Rugby, Eng.	Apr. 3, 1902
Clawson, John L.	The Clawson Company, Importers and Manufacturers of Spices, Flavoring Extracts and Grocers' Sundries, 45 S. 2nd St., Philadelphia, Pa.	Mar. 5, 1903
Coblentz, Virgil, Ph.D.	Professor of Chemistry and Physics, New York College of Pharmacy, 115 W. 68th St., New York.	Apr. 16, 1903
Coggeshall, G. W.	620 Atlantic Ave., Res. Chestnut St., Dedham, Mass.	Apr. 3, 1902
Coho, H. B.	Contracting Engineer, 114 Liberty St., New York.	Apr. 3, 1902
Coit, Chas. Welles	United Barium Co., Niagara Falls, N.Y.	Apr. 3, 1902
Coit, Dr. Jas. Milnor	St. Paul's School, Concord, N. H.	Apr. 3, 1902
Colby, Edward A.	Baker Platinum Works, Newark, N. J.	Apr. 3, 1902
Collins, C. L., 2nd	International Acheson Graphite Co., 315 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902
Cowles, Alfred H.	361 The Arcade, Res. 656 Prospect St., Cleveland, Ohio.	Apr. 3, 1902
Cox, G. E.	Superintendent Union Carbide Works, 315 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902

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		Date of election.*
Creighton, Elmer E. F.	Stanley Electric Mfg. Co., Pittsfield, Mass.	Apr. 3, 1902
Crider, J. S.	Secretary, National Carbon Company, Lock Drawer "L", Cleveland, O.	May 9, 1903
Crocker, F.B., Ph.D.	Professor of Electrical Engineering, Columbia University, Res. 14 W. 45th St., New York.	Nov. 6, 1902
Darling, J. D.,	4826 Greenaway Ave., Philadelphia, Pa.	Apr. 3, 1902
Davis, D. L.	Superintendent The Salem Electric Light and Power Co., Salem, Ohio.	Aug. 7, 1902
Davis, F. J.	Superintendent Cowles Electric Smelting and Aluminum Co., Lockport, N. Y.	Mar. 5, 1903
Deeds, Edward A.	Factory Manager, The Natural Food Company, Niagara Falls, N. Y.	Nov. 6, 1902
de Neufville, Dr. Richard	Junghofstrasse 14, Frankfurt a/M, Germany.	Feb. 5, 1903
Devine, Jos. P.	Vice-President National Battery Company, Buffalo, N. Y.	May 9, 1903
Devlin, Samuel B.	Chief Assistant and Director of Laboratory of Dr. L. Paget, 156 W. 13th St., New York.	Jan. 8, 1903
Dick, Alexander	President and Managing Director, The Delta Metal Company, 110 Cannon St., London, Eng.	Apr. 16, 1903
Dickerson, E. N.	Director and Counselor, Union Carbide Co., Stovall, N. C.	Mar. 5, 1903
Dodge, Norman	Electric Storage Battery Co., 19th St. and Allegheny Ave., Philadelphia, Pa.	Apr. 3, 1902
Doerflinger, William, F., B.S.	Chief Chemist, Acker Process Co., Niagara Falls, N. Y.	July 3, 1902
Doggett, C. S.	The Grasselli Chemical Company, East Chicago, Ind.	Apr. 3, 1902
Doney, D. C.	De Lamar Copper Refining Works, Carteret, N. J., Res. Woodbridge, N. J.	Apr. 3, 1902
Doolittle, C. E.	Manager and Electrical Engineer, The Roaring Fork Electric Light and Power Co., Aspen, Colo.	May 9, 1903
Doremus, Chas. A., M.D., Ph.D.	17 Lexington Ave., New York.	Apr. 3, 1902
Dow, Herbert H.	Midland, Mich.	Apr. 3, 1902

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		Date of election.*
Dreyfus, Dr. Wm.	Chemist and Manager, West Disinfecting Company, 162 E. 95th St., New York.	Dec. 4, 1902
Drobegg, Dr. Gustave	Charles Pfizer & Co., 81 Maiden Lane, New York, Res. 100 Dean St., Brooklyn, N. Y.	Jan. 8, 1903
Drown, T. M.	President Lehigh University, South Bethlehem, Pa.	Apr. 3, 1902
DuBois, Howard W.	501 Mariner and Merchant Building, Philadelphia, Pa.	May 9, 1903
Dudley, Dr. Chas. B.	Chemist, Pennsylvania R. R., Drawer 156, Altoona, Pa.	May 9, 1903
Dunn, Clifford E.	Counsellor-at-Law, 13-21 Park Row, New York.	Apr. 3, 1902
Durant, Edw., E.E.	115 E. 26th St., New York.	Apr. 3, 1902
Easterbrooks, F. D.	Raritan Copper Works, Perth Amboy, N. J.	Apr. 3, 1902
Eddy, A. H.	Electrician and Chemist, Eddy Electric Mfg. Co., Windsor, Conn.	Apr. 3, 1902
Edison, T. A.	Orange, N. J.	Apr. 4, 1903
Edmands, I. R.	Electrical Engineer and Superintendent Union Carbide Co., Sault Ste. Marie, Mich.	Aug. 7, 1902
Eimer, August	Eimer & Amend, 205-211 Third Ave., New York.	Dec. 4, 1902
Elliott, Arthur H.	Consolidated Gas Company, 4 Irving Place, New York.	Apr. 3, 1902
Elworthy, H. S.	Consulting Chemical Engineer, 239 Dashwood House, 9 New Broad St., London, E. C., England.	Apr. 3, 1902
Ely, Theodore N.	P. R. R. Co., Chief of Motive-Power, Broad-Street Station, Philadelphia, Pa.	Apr. 3, 1902
Emery, Arthur L.	Chemical and Mining Engineer, Indiana and 24th Sts., San Francisco, Cal.	Apr. 3, 1902
Engelhardt, Dr. Victor	Chief Chemist, Siemens-Halske Co., Vienna III, Stammgasse 12, Austria.	Dec. 4, 1902
Evans, Herbert S.	Instructor on Electrical Engineering, University of Nebraska, Lincoln, Neb.	Apr. 3, 1902
Evans, J. W.	Civil and Mining Engineer, Deseronto, Ontario, Can.	Apr. 3, 1902

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		Date of election.*
Ewin, James L.	Patent Solicitor, 900 F St., N. W., Washington, D. C.	Nov. 6, 1902
Falding, Fred. J.	Consulting Engineer, 52 Broadway, New York.	Apr. 3, 1902
Ferry, Ervin S.	Professor of Physics, Purdue University, Lafayette, Ind.	Apr. 16, 1903
Finck, Albert	Instructor in Chemistry, Case School of Applied Science, Cleveland, O., Res. 1617 Cedar Ave.	Mar. 5, 1903
FitzGerald, F. A. J.	Chemist, International Acheson Graphite Co., Niagara Falls, N. Y., P. O. Box 118.	Apr. 3, 1902
FitzGibbon, R.	77 John St., New York.	Apr. 3, 1902
Fitzmaurice, J. S.	Chief Engineer, General Post-Office, Sydney, Australia.	Apr. 3, 1902
Flanders, Louis H.	Westinghouse Machine Co., Pittsburg, Pa.	Apr. 3, 1902
Fleming, R.	General Electric Co., Lynn, Mass.	Apr. 3, 1902
Fletcher, Geo. W., E.E.	Engineer, Hadaway Electric Heating and Engineering Co., Res. 38 Grove St., Brooklyn, N. Y.	Oct. 2, 1902
Fliess, Robert A.	Superintendent, Testing Dept., Edison Storage Battery Co., Montclair, N. J., Res. 44 Chestnut St., East Orange, N. J.	Sep. 4, 1902
Foersterling, Dr. Hans	Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.	Apr. 3, 1902
Forbes, Francis	Counsellor-at-Law, 34 Nassau St., Res. 8 W. 56th St., New York.	Apr. 3, 1902
Fowler, Samuel S.	Mining Engineer, Nelson, B. C.	Apr. 3, 1902
Fraley, Jos. C.	Attorney-at-Law, 929 Chestnut St., Res. 1833 Pine St., Philadelphia, Pa.	Apr. 3, 1902
Franchot, Stanislas P.	General Manager, National Electrolytic Co., Niagara Falls, N. Y.	Sep. 4, 1902
Frankforter, Prof. G. B.	University of Minnesota, Minneapolis, Minn.	Apr. 3, 1902
Frasch, Hans A.	Consulting Chemical Engineer, 52 Broadway, New York.	May 9, 1903
Frazier, Robert T.	918 F St., N. W., Res. 3016 13th St., Washington, D. C.	Sep. 4, 1902
Freedman, W. H.	Professor of Electrical Engineering, University of Vermont, Burlington, Vt.	Apr. 3, 1902
Freeman, C. E.	Associate Professor, Electrical Department, Armour Institute, Chicago, Ill.	Nov. 6, 1902

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		Date of election.*
Frenzel, A. B.	Proprietor of Mines Containing Rare Minerals, 1540 Sherman Ave., Denver, Colo.	May 9, 1903
Fritchle, Oliver P.	Chief Chemist, Boston & Colorado Smelting Company, Argo, Colo., Res. 1618 Pennsylvania Ave., Denver, Colo.	Sep. 4, 1902
Gabriel, George A.	Box 390, Cumberland Mills, Me.	Apr. 3, 1902
Garduño, Jesus	Aguascalientes, Mexico.	Apr. 3, 1902
Garfield, A. S.	67 Ave. de Malakoff, XVI. Arrond., Paris, France.	Mar. 7, 1903
Gerry, M. H., Jr.	General Manager and Chief Engineer, Missouri River Power Co., Helena, Montana.	Apr. 3, 1902
Gibbs, Arthur E.	Chemist, The National Electrolytic Co., Niagara Falls, N. Y.	Oct. 2, 1902
Gibbs, W. T.	Director, The Electric Reduction Co., Ltd., Buckingham, Quebec.	Apr. 3, 1902
Gifford, Wm. E.	59 Emmett St., Newark, N. J.	Apr. 3, 1902
Gilchrist, Peter S.	Chemical Engineer, Charlotte, N. C.	Apr. 3, 1902
Ginder, W. H. H.	American Sheet Steel Co., Vandergrift, Pa.	Apr. 3, 1902
Gladson, Prof. W.N.	Electrical Engineering Dpt., University of Arkansas, Fayetteville, Ark.	Apr. 3, 1902
Goddard, Chris. M.	National Board of Fire Underwriters, 55 Kilby St., Boston, Res. 1008 Beacon St., Newton Centre, Mass.	Apr. 3, 1902
Goldsborough, W. E.	Chief of Electricity Department, World's Fair, St. Louis, Mo., Res. Lafayette, Ind.	Nov. 6, 1902
Goldschmidt, Dr. V.	Professor of Mineralogy, Gaisbergstrasse 9, Heidelberg, Germany.	Jan. 8, 1903
Goodrich, C. C.	Assistant General Superintendent, The B. F. Goodrich Co., Akron, Ohio.	Apr. 3, 1902
Goodwin, H. M., Ph.D.	Massachusetts Institute of Technology, Boston, Mass.	Apr. 3, 1902
Goodwin, W. L. Ph.D.	Director School of Mining, Kingston, Ont., Can.	Apr. 3, 1902
Gordon, Prof. C. McC.	Central University of Kentucky, Danville, Ky.	Apr. 3, 1902
Granbery, J. H.	561 Walnut St., Elizabeth, N. J.	Apr. 3, 1902

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		Date of election.*
Granja, Rafael	Chemical Engineer, President Ceres Chemical Co., Kingston, N. Y., Box 799.	Apr. 3, 1902
Graves, Walter G.	Superintendent, The Grasselli Chemical Co., Res. 850 Willson Ave., Cleveland, O.	Mar. 5, 1903
Greenstreet, C. J.	Chemist, Pittsburgh Plate Glass Co., Ford City, Pa.	Nov. 6, 1902
Gruner, Henry E.	Civil Engineer, The Laufenburger Wasserkraft Gewinnung, 9 Nauenstrasse, Basel, Switzerland.	July 3, 1902
Guye, Prof. P. A.	3 Chemin des Cottages, Florissant, Geneve, Switzerland.	Dec. 4, 1902
Haber, Prof. Fritz, Ph.D.	Technische Hochschule, Karlsruhe, Germany.	Nov. 6, 1902
Hadley, A. N.	Box 33, Indianapolis, Ind.	Apr. 3, 1902
Haggott, Ernest A.	Manager Arizona Blue Bell Copper Co., Mayer, Ariz.	Apr. 3, 1902
Hall, Charles M.	Pittsburgh Reduction Co., Res. 136 Buffalo Ave., Niagara Falls, N. Y.	Apr. 3, 1902
Hall, Jos. B.	General Electric Company, Res. 621 W. 65th Place, Chicago, Ill.	Feb. 5, 1903
Hall, S. F.	Superintendent, Norton Emery Wheel Co., Niagara Falls, N. Y.	Apr. 16, 1903
Hambuechen, Carl, E.E.	Electrochemist, 616 Lake St., Madison, Wis.	Apr. 3, 1902
Hamilton, Louis P.	Dunbar, Pa.	Apr. 3, 1902
Hammerschmidt, Dr. Richard	Director der Accumulatoren Werke, System Pollak, Mainzerlandstr. 259, Frankfurt a/M, Germany.	Jan. 8, 1903
Hance, Anthony M.	Hance Bros. & White, Philadelphia, Pa.	Apr. 3, 1902
Hanchett, Geo. T.	Electrical and Mechanical Engineer, 116 Nassau St., New York.	Apr. 3, 1902
Harper, Dr. Henry Winston	University of Texas, Res. Cor. 23rd and San Antonio Sts., Austin, Tex.	Apr. 3, 1902
Harrington, Edwin I., M.D.	87 N. Broadway, Yonkers, N. Y.	Apr. 3, 1902
Harris, J. W.	Elkins Park, Montgomery County, Pa. Box 210.	Apr. 3, 1902
Harris, W. D.	3609 Ludlow St., Philadelphia, Pa.	Apr. 3, 1902
Hart, Ed., Ph.D.	Professor of Chemistry, Lafayette College, Easton, Pa.	Aug. 7, 1902
Hart, Walter H.	2010 Wallace St., Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Harvey, E. F.	St. Johns, Newfoundland.	Apr. 3, 1902
Haskell, F. W.	President The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Haslwanter, Chas.	908 Willoughby Ave., Brooklyn, N. Y.	Apr. 3, 1902
Hatzel, J. C.	114 Fifth Ave., New York.	Apr. 3, 1902
Havemeyer, H. O., Jr.	117 Wall St., New York, Res. Mahwah, N. J.	Apr. 16, 1903
Hay, Arthur M.	4041 Walnut St., Philadelphia, Pa.	Apr. 3, 1902
Heath, H. E.	Eddy Electric Mfg. Co., Windsor, Conn.	Apr. 3, 1902
Heckman, J. Conrad	Larkin Soap Mfg. Co., Buffalo, N. Y.	Apr. 3, 1902
Herbert, C. G.	Mechanical Engineer, 303 Hubbard Ave., Detroit, Mich.	Oct. 2, 1902
Hering, Carl	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Herzog, F. Benedict	Herzog Teleseme Co., 51 W. 24th St., New York.	Apr. 3, 1902
Higgins, Aldus C., C.S.	Norton Emery Wheel Co., Worcester, Mass.	Sep. 4, 1902
Higgins, Francis W.	Assistant Chemist, The Carborundum Co., Res. 549 Fourth St., Niagara Falls, N. Y.	Feb. 5, 1903
Hitchcock, Halbert K.	Experimental Engineer, The Pittsburgh Plate Glass Co., Floreffe, Pa.	Oct. 2, 1902
Hite, B. H.	West Virginia Experiment Station, Morgantown, W. Va.	Apr. 3, 1903
Hobbs, Perry L., Ph.D.	Western Reserve Medical College, Cor. Erie and St. Clair Sts., Cleveland, Ohio.	Apr. 3, 1902
Hofmann, Ottokar	Southwest Chemical Co., Argentine, Kans.	Apr. 3, 1902
Holman, G. U. G	Canadian Electric Light and Power Co., Ltd., 83 Dalhousie St., Quebec, Can.	Apr. 3, 1902
Hopkins, Prof. Nevil Monroe	Columbian University, 1730 I St., N. W., Washington, D. C.	Apr. 3, 1902
Horry, Wm. S.	Consolidated Lake Superior Power Co., Niagara Falls, N. Y.	Feb. 5, 1903
Hoskins, Wm.	81 S. Clark St., Chicago, Ill., Res. La Grange, Ill.	Apr. 3, 1902
Houston, Edwin J., Ph.D.	1203 Crozier Building, Res. 1809 Spring Garden St., Philadelphia, Pa. Phone 1-27-12, Cable address "Volta."	Oct. 2, 1902

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		Date of election.*
Howard, Henry	175 Mountfort St., Brookline, Mass.	Apr. 3, 1902
Howard, Geo. M.	Electric Storage Battery Co., Res. 2220 Venango St., Philadelphia, Pa.	Apr. 3, 1902
Howard, Prof. S. F.	Department of Chemistry, Massachusetts Agricultural College, Res. 66 Pleasant St., Amherst, Mass.	Apr. 3, 1902
Howe, Henry M., A.M.	27 W. 73rd St., New York, Professor of Metallurgy, Columbia University.	Aug. 7, 1902
Huddle, W. J.	University of Wisconsin, Res. 604 Francis St., Madison, Wis.	Apr. 3, 1902
Hunt, A. M.	Consulting Engineer, 331 Pine St., San Francisco, Cal.	Apr. 3, 1902
Hunter, Thomas G.	630 Real Estate Trust Building, Broad and Chestnut Sts., Philadelphia, Pa.	Apr. 3, 1902
Hutchinson, Edw. J.	Vice-President, Taylor Chemical Co., 1245 E. 3rd St., Cincinnati, Ohio.	Apr. 3, 1902
Hutchinson, Rowland W., Jr.	Polytechnic Institute, Res. 294 Clinton St., Brooklyn, N. Y.	Apr. 3, 1902
Hutton, R. S., M.Sc.	Lecturer on Electrochemistry, Owens College, Manchester, Eng.	Apr. 3, 1902
Ihlder, J. D., M.E.	Electrical Engineer, Yonkers, N. Y.	Apr. 3, 1902
Irvine, H. A.	Oldbury Electro-Chemical Co., Niagara Falls, N. Y.	Apr. 3, 1902
Isaacs, A. S., Ph.M.	Pennsylvania Malleable Co., KcKees Rocks, Pa., Res. 1214 Sheffield St., Allegheny, Pa.	Apr. 3, 1902
Isakovics, Alois von	Herbene Scientific Laboratories, 449 E. 121st St., New York.	Apr. 3, 1902
Jackson, Dugald C.	Consulting Engineer, Professor of Electrical Engineering, University of Wisconsin, Madison, Wis.	Apr. 3, 1902
Jackson, John Price, B.S., E.E., M.E.	Professor of Electrical Engineering, State College, Pa.	Oct. 2, 1902
James, J. H.	Lake Superior Power Co., Sault Ste. Marie, Ont., Can.	Apr. 3, 1902
Jenks, W. J.	120 Broadway, N. Y.	Apr. 3, 1902
Jeppson, George N.	Norton Emery Wheel Co., Worcester, Mass.	Sep. 4, 1902
Johnson, F. C.	Chemist, National Acid Co., 714 Union St., New Orleans, La.	Apr. 3, 1902

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		Date of election.*
Johnson, Woolsey McA.	69 Vernon St., Hartford, Conn.	Apr. 3, 1902
Johnston, Thos. J.	Counsellor-at-Law, 11 Pine St., Res. 228 Willoughby Ave., New York.	Apr. 3, 1902
Jones, L. J. W.	Tacoma Smelting Co., Tacoma, Wash.	Apr. 3, 1902
Kahlbaum, Prof. Geo., Ph.D.	Basel, Switzerland.	Apr. 3, 1902
Kahlenberg, Louis, Ph.D.	Professor of Physical Chemistry, University of Wisconsin, Res. 306 Lake St., Madison, Wis.	Apr. 3, 1902
Keith, Dr. N. S.	Electro-Metallurgist and Mining Engineer, Room 505, 95 Liberty St., New York.	Apr. 3, 1902
Keller, Edward	P. O. Box 724, Baltimore, Md.	Apr. 3, 1902
Kelley, J. F., Ph.D.	Stanley Electric Mfg. Co., 284 W. Housatonic St., Pittsfield, Mass.	Apr. 3, 1902
Kellner, Carl, Ph.D.	Hohe Warte 29, Vienna, Austria.	Jan. 8, 1903
Kenan, Wm. R., Jr.	Assistant Manager, Traders Paper Co., Lockport, N. Y.	Apr. 3, 1902
Kennedy, J. J.	Engineer, 52 Broadway, New York.	May 9, 1903
Kennelly, Arthur E., D.Sc.	Professor of Electrical Engineering, Pierce Hall, Harvard University, Cambridge, Mass.	Nov. 6, 1902
Kenyon, Wm. H.	49 Wall St., New York.	Apr. 3, 1902
Kern, Edward F.	Betts Laboratory, Res. 559 Second Ave., Lansingburgh, N. Y.	Apr. 4, 1903
Kintner, C. J.	Solicitor of Patents, 45 Broadway, New York.	Apr. 3, 1902
Kitsee, Dr. Isador	306 Stock Exchange Place, Philadelphia, Pa.	Apr. 3, 1902
Klipstein, Ernest C.	122 Pearl St., New York, P. O. Box 2833, Res. 116 Prospect St., East Orange, N. J.	Apr. 3, 1902
Knapp, Geo. O.	Vice-President, Union Carbide Co., Res. 157 Michigan Ave., Chicago, Ill.	Nov. 6, 1902
Knorr, Aug. E.	Baltimore Copper Smelting and Rolling Co., Baltimore, Md.	Apr. 4, 1903
Knox, W. J.	Copperfield, Vt.	Apr 3, 1902
Knudson, A. A.	Electrical Engineer, 34 Nassau St., Res. 758 Putnam Ave., Brooklyn, N. Y.	Nov. 6, 1902

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		Date of election.*
Krebs, A. Sonnin	Krebs Pigment and Chemical Co., Newport, Del., Res. 806 Franklin St., Wilmington, Del.	Apr. 3, 1902
Kyle, T. D.	106 E. 5th St., Leadville, Colo.	Apr. 3, 1902
Lacey, Frank H.	Colorado Iron Works Co., Denver, Colo.	Apr. 3, 1902
Lafore, J. A.	119 S. 11th St., Res. 6368 Drexel Road, Philadelphia, Pa.	Apr. 3, 1902
Landis, Walter S.	Assistant in Department of Metallurgy, Lehigh University, Res. 48 Church St., Bethlehem, Pa.	Dec. 4, 1902
Landolt, Dr. Hans	Turgi, Switzerland.	Feb. 5, 1903
Langley, John W., Ph.D.	Case School of Applied Science, Res. 77 Cornell St., Cleveland, O.	Apr. 3, 1902
Langton, John	Consulting Engineer, 99 John St., New York.	Apr. 3, 1902
Lansingh, V. R.	The V. R. Lansingh Co., Illuminating and Electrical Engineers, 18 E. Adams St., Res. 5329 Kimbark Ave., Chicago, Ill.	Apr. 4, 1903
Larchar, Arthur B.	Penobscot Chemical Fibre Co., Great Works, Me.	Apr. 3, 1902
Lathwood, Arthur	Chemist, Oldbury Electro-Chemical Co., Box 238, Niagara Falls, N. Y., Res. La Salle, Niagara Falls, N. Y.	Aug. 7, 1902
Laughlin, W. C.	Assayer, Chemist and Mining Engineer, Ouray, Colo., Box 1117.	Apr. 3, 1902
Leavitt, E. D.	2 Central Square, Cambridge, Mass.	Apr. 3, 1902
Lee, F. V. T.	Electrical Engineer, Vice-President and General Manager, John Martin & Co., Electrical Contractors and Engineers, 31 and 33 New Montgomery St., San Francisco, Cal.	Apr. 3, 1902
Lee, Waldemar	Chemist, New Jersey Zinc Co., Palmerton, Carbon Co., Pa.	Apr. 3, 1902
Lenher, V., Ph.D.	148 W. Gorham St., Madison, Wis.	Apr. 3, 1902
Levine, Edmund J.	The Fibroid Co., 636-638 Broadway, New York.	Apr. 3, 1902
Lichthardt, G	1800 M St., Box 510, Sacramento, Cal.	Apr. 3, 1902
Lincoln, A. T., Ph.D.	Instructor in Chemistry, University of Illinois, Urbana, Ill.	Nov. 6, 1902
Lincoln, P. M.	Westinghouse Electric and Manufacturing Co., Pittsburg, Pa.	Apr. 3, 1902

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		Date of election.*
Lloyd, M. G., Ph.D.	National Bureau of Standards, Washington, D. C.	Apr. 3, 1902
Lockwood, Chas. E.	439 E. 144th St., New York.	Apr. 3, 1902
Loeb, Morris	37 E. 38th St., and New York University, New York	Apr. 3, 1902
Long, Frederick H.	Consulting Metallurgical and Contracting Engineer, 84 Adams St., Res. 2110 Clarendon Ave., Chicago, Ill.	Apr. 3, 1902
Loomis, Prof. E. H.	Princeton, N. J.	Apr. 3, 1902
Lorenz, Prof. Richard, Ph.D.	V. Moussonstrasse, Zurich, Switzerland.	Sep. 4, 1902
Lovejoy, D. R. B.S., E.E.	Electrical Engineer, Superintendent Atmospheric Products Co., Niagara Falls, N. Y.	Apr. 3, 1902
Lyman, James	Assistant Engineer, General Electric Co., Monadnock Building, Chicago, Ill.	Apr. 3, 1902
Lyndon, Lamar	Consulting Electrical Engineer, Park Row Building, Res. 243 W. 98th St., New York.	Apr. 3, 1902
Mabery, Prof. C. F.	Case School of Applied Science, Cleveland, O.	Mar. 5, 1903
MacFadden, C. K.	Geneva, Ind.	Apr. 3, 1902
MacMahon, James	Castner Electrolytic Alkali Co., Superintendent Bleaching Powder Department, Niagara Falls, N. Y.	Aug. 7, 1902
Machalske, Dr. F. J.	P. O. Box 25, Sta. W., Brooklyn, N. Y.	Dec. 4, 1902
MacNutt, Barry, E.E., M.S.	Physical Laboratory Lehigh University, Res. 27 S. Linden St., Bethlehem, Pa.	Apr. 3, 1902
Magnus, Benj., E.E.	Assistant Superintendent, Electrolytic Refinery and Silver Mill of the Anaconda Copper Mining Co., Res. Montana Hotel, Anaconda, Mont.	Apr. 3, 1902
Mailloux, C. O.	76 William St., New York.	Apr. 3, 1902
Main, Wm.	Engineer and Chemist, 299 Jefferson Ave., Brooklyn, N. Y.	Apr. 3, 1902
Marks, Prof. W. D.	The Art Club, Philadelphia, Pa.	Apr. 3, 1902
Mathews, Wm. O.	The National Carbon Co., Dover Bay, Ohio.	Nov. 6, 1902

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		Date of election.*
Marvin, A. B., Jr.	Patent Office, Washington, D. C.	Apr. 3, 1902
Mauran, Max	Engineer and Assistant Manager, Castner Electrolytic Alkali Co., Niagara Falls, N. Y.	Nov. 6, 1902
Maynard, Geo. W.	20 Nassau St., New York.	Apr. 3, 1902
Maywald, Fred. J.	Chemist, 80 Broad St., New York, Res. 1028 72nd St., Brooklyn, N. Y.	Apr. 3, 1902
McConnell, Jacob Y.	500 Broad St., Philadelphia, Pa., Res. Colwyn, Pa.,	Apr. 3, 1902
McCoy, W. Asa	Raritan Copper Works, Res. 57 Kearney St., Perth Amboy, N. J.	Apr. 3, 1902
McIntosh, Prof. D.	Demonstrator in Physical Chemistry, McGill University, Montreal, Can.	Dec. 4, 1902
McKeown, W. W., Jr.	718 Wick Ave., Youngstown, O., Tennessee Coal, Iron and Railroad Co., Oxmoor, Ala.	Apr. 3, 1902
McKittrick, F. J. A.	Engineer, Power and Mining Department General Electric Co., 44 Broad St., New York.	Nov. 6, 1902
McMillin, Francis C.	Counsellor-at-Law, 1609 Williamson Building, Res. 2128 Euclid Avenue, Cleveland, O.	Apr. 16, 1903
McNeill, Ralph	510 W. 23rd St., Res. 223 W. 106th St., New York.	Feb. 5, 1903
Melcher, Arthur C.	58 Bowen St., Newton Centre, Private Assistant to Dr. W. R. Whitney, Massachusetts Institute of Technology, Boston, Mass.	July 3, 1902
Meldrum, Archibald	Chemist, P. O. Box 144, Savannah, Ga.	May 9, 1903
Merz, Chas. H.	Consulting Engineer, 28 Victoria St., Westminster, London, S. W., and 1 Mosley St., Newcastle-upon-Tyne, Eng.	Apr. 3, 1902
Metz, H. A.	122 Hudson St., New York.	Apr. 3, 1902
Miller, Dr. W. Lash	University of Toronto, Res. 50 St. Albans St., Toronto, Can.	Apr. 3, 1902
Mills, Dr. J. E.	Instructor in Physical Chemistry, University of North Carolina, Chapel Hill, N. C.	Apr. 16, 1903
Molera, E. J.	Civil Engineer, 606 Clay St., San Francisco, Cal.	Apr. 3, 1902
Monell, A.	President, International Nickel Co., 74 Broadway, New York.	Apr. 3, 1902
Morehead, J. M.	157 Michigan Ave., Chicago, Ill.	Feb. 5, 1903

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		Date of election.*
Morehead, J. T.	99 Cedar St., President The Willson Aluminum Co., New York.	Apr. 4, 1903
Morgan, J. L. R., Ph.D.	Columbia University, New York.	Apr. 3, 1902
Moritz, C. H	Pittsburgh Reduction Co., Niagara Falls, N. Y.	Apr. 4, 1903
Morris, Henry G.	408 Bourse Building, Philadelphia, Pa.	Apr. 3, 1902
Morrison, W. J., Jr., M.S.	60-62 Broadway, New York, Res. Ridgefield Park, N. J.	Apr. 3, 1902
Moses, Herbert B.	National Battery Co., 366-382 Massachusetts Ave., Buffalo, N. Y.	Apr. 3, 1902
Mott, W. R., B.S.,	921 University Ave., Madison, Wis.	Mar. 5, 1903
Mullin, E. H.	General Electric Co., 44 Broad St., New York.	Apr. 3, 1902
Murphy, Edwin J.	The British Thomson-Houston Co., Ltd., Rugby, Eng.	Oct. 2, 1902
Nadolsky, W. L.	Student Electrical Engineering, Columbia University, 110 Chrystie St., New York.	May 9, 1903
Nakayama, T.	Burgess Sulphite Fibre Co., Berlin, N.H., Res. Kochi, Japan, associated with Imperial Japanese Government.	Feb. 5, 1903
Nichols, W. Standish	Westinghouse Electric and Manufacturing Co., Pittsburg, Res. 835 Rebecca Ave., Wilkinsburg, Pa.	Apr. 3, 1902
Norden, Konrad Ph.D.	Burggrafenstr. 15, Berlin, W., Germany.	Apr. 3, 1902
Norman, Geo. M.	General Chemical Co., 517 Cooper St., Camden, N. J.	Apr. 3, 1902
Nunn, Dr. Richard J.	5 York St., E., Savannah, Ga.	Apr. 3, 1902
Oliver, Frank M.	Chemist, H. K. Mulford Co., 755 N. 38th St., Philadelphia, Pa.	Apr. 3, 1902
Osborne, Loyall A.	Westinghouse Electric and Manufacturing Co., Pittsburg, Pa.	Apr. 3, 1902
Osterberg, Max, E.E., A.M.	Consulting Electrical and Mechanical Engineer, 11 Broadway, New York.	Apr. 3, 1902
Paget, Dr. Leonard	Electrochemist and Chemical Engineer, P. O. Box 397, Res. 80 Greenwich St., New York.	Dec. 4, 1902
Palmer, Prof. Chase	Professor of Chemistry, Central University of Kentucky, Danville, Ky.	Apr. 3, 1902

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		Date of election.*
Palmer, E. Carlton, D.D.S.	1311 N. Broad St., Philadelphia, Pa.	Apr. 3, 1902
Park, Edgar	General Manager, St. Lawrence River Power Co., Hanover Bank Building, New York, Res. Larchmont, N. Y.	Apr. 16, 1903
Parsons, Louis A., Ph.D.	Johns Hopkins University, Baltimore, Md.	Apr. 3, 1902
Patten, Harrison E., Ph.D.	Instructor in General Chemistry, Chemical Laboratory, University of Wisconsin, Res. 1109 University Ave., Madison, Wis.	Apr. 3, 1902
Patterson, Geo. W., Jr., Ph.D.	Junior Professor of Electrical Engineering, University of Michigan, Res. 814 S. University Ave., Ann Arbor, Mich.	Nov. 6, 1902
Pattison, Frank A.	Consulting Engineer, 141 Broadway, New York.	Apr. 3, 1902
Paul, Henry N., Jr.	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Pease, Harold C.	Engineer, General Electric Co., Res. 820 Union St., Schenectady, N. Y.	Nov. 6, 1902
Pepper, David, Jr., M.E.	Contracting Engineer, Pepper & Register, 112 N. Broad St., Res. 1826 Spruce St., Philadelphia, Pa.	July 3, 1902
Perkin, Frederick Mollwo, Ph.D.	Professor of Chemistry, Borough Polytechnic Institute, 103 Borough Road, London, S. E., Res. 5 Tyson Road, Forest Hill, London, E. C., Eng.	Sep. 4, 1902
Perkins, Frank C.	Electrical Engineer, 126 Erie County Bank Building, Buffalo, N. Y.	Apr. 3, 1902
Perry, R. S.	5104 Pulaski Ave., Germantown, and Harrison Bros. & Co., Philadelphia, Pa.	Apr. 3, 1902
Petty, Walter M.	Consulting Electrician, Superintendent Fire Alarm, 160 Orient Way, Rutherford, N. J.	Apr. 3, 1902
Peyton, W. C.	Martinez, Contra Costa Co., California.	Apr. 3, 1902
Phillips, Wm. B.	Director of the Mineral Survey, University Station, Austin, Tex.	Mar. 5, 1903
Pickering, Oscar W.	Teacher of Chemistry, Massachusetts Institute of Technology, Res. 52 Clifton St., Melrose Highlands, Mass.	Oct. 2, 1902
Piltschikoff, Prof. Nicolas	Professor of Physics, Technological Institute, Kharkov, Russia.	Sep. 4, 1902

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		Date of election.*
Pinkerton, Andrew	Electrician, American Sheet Steel Co., Vandergrift, Pa., Box 19.	Apr. 3, 1902
Pond, G. G., Ph.D.	Professor of Chemistry, State College, Pa.	July 3, 1902
Poole, Cecil P.	Editor, American Electrician, 114 Liberty St., New York.	Apr. 3, 1902
Poole, Herman	Chemist and Metallurgist, 157 W. 106th St., New York.	May 9, 1903
Porter, John L.	Laboratory of Sewerage and Water Board, 602 Carondelet St., Res. 1317 Henry Clay Ave., New Orleans, La.	Apr. 3, 1902
Potter, Henry Noel	510 W. 23rd St., New York, Res. Rochelle Park, New Rochelle, N. Y.	Apr. 3, 1902
Powell, Thomas H.	South Norwalk, Conn.	Apr. 3, 1902
Pratt, Frederick S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Pretzfeld, Dr. C. J.	P. O. Box 305, Chemist, The National Electrolytic Co., Niagara Falls, N. Y.	Dec. 4, 1902
Price, Edgar F.	Manager, Union Carbide Co., Niagara Falls, N. Y.	July 3, 1902
Rankine, Wm. B.	Niagara Falls Power Company, Niagara Falls, N. Y.	Apr. 4, 1903
Rau, Prof. Albert G.	Superintendent, Moravian Parochial School, Bethlehem, Pa.	Apr. 3, 1902
Reber, Samuel	Lieutenant-Colonel and Military Secretary, Headquarters of the Army, Washington, D. C.	Apr. 3, 1902
Reckhart, D. W.	Cor. San Francisco and Chihuahua Sts., El Paso, Tex.	Apr. 3, 1902
Recklinghausen, M. von, Ph.D.	11 E. 24th St., New York.	Apr. 3, 1902
Reed, C. J.	3313 N. 16th St., Philadelphia, Pa.	Apr. 3, 1902
Reed, Mrs. M. J.	3313 N. 16th St., Philadelphia, Pa.	Oct. 2, 1902
Reuterdahl, Arvid	20 Babcock St., Providence, R. I.	Apr. 3, 1902
Reynolds, F. G.	368 St. Nicholas Ave., New York.	Apr. 3, 1902
Rhodin, B. E. F.	Chief Engineer, Canadian Electro-Chemical Co., Ltd., Sault Ste. Marie, Ont., Can.	Apr. 3, 1902
Richards, Jos. W., Ph.D.	Lehigh University, Bethlehem, Pa.	Apr. 3, 1902

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		Date of election.*
Ries, Elias E.	Consulting Electrical Engineer, 116 Nassau St., New York.	Apr. 3, 1902
Riker, John J.	Treasurer, Oldbury Electrochemical Co., 46 Cedar St., New York.	Mar. 5, 1903
Roberts, Isaiah L.	Director, Roberts Chemical Co., 40 Wall St., New York.	Oct. 2, 1902
Roberts, J. C.	Treasurer, Atmospheric Products Co., 53 Gluca Building, Niagara Falls, N. Y.	Oct. 2, 1902
Robbins, W. A.	535 Bailey St., Camden, N. J.	Apr. 3, 1902
Robinson, Almon	P. O. Box 54, Lewiston, Me.	Apr. 3, 1902
Rochlitz, Prof. Oscar A.	Armour Institute of Technology, 623 Haddon Ave., Chicago, Ill.	Apr. 3, 1902
Rodgers, Ashmead G.	Assistant Superintendent, The Carborundum Co., Niagara Falls, N. Y.	Nov. 6, 1902
Rodman, Hugh	Electric Storage Battery Co., 19th and Allegheny Ave., Philadelphia, Pa.	Apr. 3, 1902
Roeber, E. F., Ph.D.	929 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902
Roepper, C. W.	Mt. Airy Station, Philadelphia, Pa.	Apr. 3, 1902
Rogers, A. J.	318 Ogden Ave., Teacher of Physical Chemistry, South Division High School, Milwaukee, Wis.	Feb. 5, 1903
Roller, F. W.	Electrical Instruments (Machado & Roller), 203 Broadway, New York.	Apr. 3, 1902
Roller, H. C.	The Port Chester Chemical Co., Port Chester, N. Y.	Apr. 3, 1902
Rollins, Wm.	250 Marlborough St., Boston, Mass.	Apr. 3, 1902
Rosebrugh, Prof. T. R.	School of Practical Science, Toronto, Can.	Apr. 3, 1902
Rosendale, O. M.	Consulting Metallurgist, Mining Engineer, 515-516 Oregonian Building, Portland, Ore.	Apr. 3, 1902
Ross, G. McM.	Virginia City, Nev.	Apr. 3, 1902
Rossi, A. J.	35 Broadway, New York.	Apr. 3, 1902
Rowand, Lewis G.	Wetherill Separating Co., Clover and Ferguson Sts., Newark, N. J., Res. 130 N. Maple Ave., East Orange, N. J.	Apr. 3, 1902
Rowland, Arthur J.	Professor of Electrical Engineering, Drexel Institute, Res. 4510 Osage Ave., Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Russell, Chas. J.	General Superintendent, Suburban Electric Co., 4510 Frankford Ave., Philadelphia, Pa.	Apr. 3, 1902
Rushmore, David B.	Stanley Electric Manufacturing Co., Pittsfield, Mass.	Apr. 3, 1902
Ruthenberg, Marcus	1716 N. Broad St., Philadelphia, Pa., Balton House, Harrisburg, Pa., Pennsylvania Steel Co., Lebanon, Pa.	Apr. 3, 1902
Sadtler, Samuel P., Ph.D.	N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.	Apr. 3, 1902
Sadtler, Samuel S.	N. E. Cor. 10th and Chestnut Sts., Philadelphia, Pa.	Apr. 3, 1902
Salom, Pedro G.	408 Bourse Building, Philadelphia, Pa.	Apr. 3, 1902
Saunders, Prof. A. P.	Hamilton College, Clinton, N. Y.	Apr. 3, 1902
Schlegel, J. W.	602 E. 5th St., New York.	Feb. 5, 1903
Schlesinger, Bart. E.	The Merrimack Chemical Co., Res. 92 Mt. Vernon St., Boston, Mass.	Nov. 6, 1902
Schoonmaker, H.	734 W. 9th St., Cincinnati, O.	Apr. 3, 1902
Schreiter, Henry	Counsellor-at-Law, 20 Nassau St., New York.	Apr. 3, 1902
Seeger, L.	P. O. Box 957, Res. 52 Broadway, New York.	Feb. 5, 1903
Seward, Geo. F.	The Willson Aluminum Co., 99 Cedar St., New York.	Apr. 4, 1903
Seward, Geo. O.	The Wilson Aluminum Co., Holcomb Rock, Va.	Apr. 3, 1902
Shattuck, A. F.	The Solvay Process Co., Detroit, Mich.	Apr. 3, 1902
Shaw, Edwin C.	The B. F. Goodrich Co., Akron, Ohio, Res. 104 Park St.	Apr. 3, 1902
Shaw, Howard B.	Professor of Electrical Engineering, University of Missouri, Columbia, Mo.	Apr. 3, 1902
Sheldon, Samuel, A.M., Ph.D.	Professor of Physics and Electrical Engineering Polytechnic Institute, Brooklyn, N. Y.	Apr. 3, 1902
Shepherd, E. S.	205 Hazen St., Ithaca, N. Y., Res. Remington, Ind.	Apr. 3, 1902
Shepherd, Lee	Dow Chemical Co., Midland, Mich.	Mar. 5, 1903
Shields, Dr. John	Private Research Chemist, 4 Stanley Gardens, Willesden Green, London, N. W., Eng.	Dec. 4, 1902

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		Date of election.*
Shorey, Edmund C.	1802 King St., P. O. Box 360, Honolulu, Hawaiian Islands.	Apr. 3, 1902
Skelton, H. A.	Assistant Engineer, The British Aluminum Co., Foyers (Lochness), N. B., Scotland.	Apr. 4, 1903
Skinner, Hervey J.	15 Chestnut St., Wakefield, Mass.	Apr. 3, 1902
Smith; Prof. A. W.	Case School of Applied Science, Res. 1101 E. Madison Ave., Cleveland, Ohio.	Apr. 3, 1902
Smith, E. A. C.	Metallurgist, Baltimore Copper Smelting and Rolling Co., Baltimore, Res. Roland Park, Md.	May 9, 1903
Smith, Edmund S.	The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Smith, Edward W.	Electric Storage Battery Co., 19th St. and Allegheny Ave., Res. 5317 Germantown Ave., Philadelphia, Pa.	Apr. 3, 1902
Smith, F. Warren	Agent California Powder Works, Res. Los Catos, Santa Clara Co., Cal.	May 9, 1903
Smith, S. N.	North Shore Reduction Company, Res. 725 Temple Court, Minneapolis, Minn.	Apr. 4, 1903
Smith, Wm. Lincoln	Concord, Mass.	Apr. 3, 1902
Snelling, W. O.	Columbian University, Res. 3412 13th St., N. W., Washington, D. C.	Oct. 2, 1902
Speiden, Clement C.	Summit, N. J., and 122 Pearl St., New York.	Nov. 6, 1902
Sperry, Elmer A.	855 Case Ave., Cleveland, O.	Apr. 3, 1902
Stalnaker, E. S.	Box 575, Morgantown, W. Va.	Apr. 3, 1902
Stansfield, Prof. A.	Professor of Metallurgy, McGill University, Montreal, Can.	Jan. 8, 1903
Stearns, Theron C.	Consulting Chemist, 44 Montgomery St., Jersey City, N. J.	Jan. 8, 1903
Steere, Thomas E., A.B.	Castner Electrolytic Alkali Co., Niagara, Falls, N. Y.	Aug. 7, 1902
Stein, Emanuel	General Manager, Electro Gas Co., 45 Broadway, New York.	May 9, 1903
Stein, Walter M.,	President and General Manager, Primos Chemical Co., Primos, Delaware Co., Pa.	Jan. 8, 1903
Steinmetz, Chas. P.	General Electric Co., Res. Wendell Ave., Schenectady, N. Y.	Aug. 7, 1902

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		Date of election.*
Steinmetz, Jos. A.	Janney and Steinmetz Co., 826 Drexel Building, Philadelphia, Pa.	Apr. 3, 1902
Stone, Chas. A.	Stone & Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Sweet, H. N.	50 Beacon St., Boston, Mass.	Apr. 3, 1902
Taggart, Walter T.	Instructor in Organic Chemistry, University of Pennsylvania, Res. 730 N. 20th St., Philadelphia, Pa.	Nov. 6, 1902
Taylor, Edward R.	Penn Yan, N. Y.	Apr. 3, 1902
Taylor, M. Temple	Manufacturer of Camphor by Electrochemical Process, Savannah, Ga.	May 9, 1903
Terven, Lewis A.	6345 Marchand St., Pittsburg, Pa.	Apr. 3, 1902
Tesla, N.	46 and 48 E. Houston St., New York.	Apr. 3, 1902
Thelberg, John, M.D.	45 W. 32nd St., New York.	Apr. 3, 1902
Thomas, Chas. W.	Secretary Reebel Paper and Lithograph Co., Nutley, N. J.	July 3, 1902
Thomas, J. W	Hokendauqua, Pa.	Apr. 3, 1902
Thompson, Robt. M.	74 Broadway, New York.	Apr. 3, 1902
Thowless, O. M.	P. O. Box 273, Newark, N. J.	Feb. 5, 1903
Threlfall, Richard	30 George Road, Birmingham, Eng.	Apr. 4, 1903
Tillberg, Erik W.	Westervik, Sweden.	Nov. 6, 1902
Tone, F. J.	Superintendent, The Carborundum Co., Niagara Falls, N. Y.	Apr. 3, 1902
Townsend, C. P.	918 F St., N. W., Washington, D. C.	Apr. 3, 1902
Ulke, Titus	New York and Pennsylvania Highland Paper Co., Johnsonburg, Elk Co., Pa.	Apr. 3, 1902
Vander Naillen, A.	The A. Vander Naillen School of Engineering, 113 Fulton St., San Francisco, Cal.	Apr. 3, 1902
Van Winkle, Abr.	The Hanson & Van Winkle Co., 35 Lincoln Park, Newark, N. J.	Jan. 8, 1903
Vaughn, Chas. F.	Superintendent, Castner Electrolytic Alkali Co., Niagara Falls, N. Y.	Nov. 6, 1902
Vicarey, Robert W.	Works Manager and Analyst, W. O. Rooper & Co., Storage Battery Makers, Victoria Works, Eastgate St., Stafford, Eng.	Dec. 4, 1902
Vincent, Jos. A.	421 Chestnut St., Philadelphia, Pa.	Apr. 3, 1902

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		Date of election.*
Voege, Adolph L.	Technische Hochschule, Zurich, Switzerland.	Apr. 3, 1902
Vogel, G. C.	Pfister & Vogel, Milwaukee, Wis.	Apr. 3, 1902
Volney, C. W.	173 W. 81st St., New York.	Apr. 3, 1902
Voorhees, Louis A.	P. O. Box 357, New Brunswick, N. J.	Apr. 3, 1902
Vorce, Loren R.	Suite 29, 509 Russell Ave., Cleveland, Ohio.	Oct. 2, 1902
Wagner, Henry L., M.D., Ph.D.	Professor Laryngology, University of California, 522 Sutter St., San Francisco, Cal.	Apr. 3, 1902
Wagner, Prof. J., Ph.D.	Leipzig, Mozartstrasse 7, Germany.	Dec. 4, 1902
Wahl, W. H., Ph.D.	Secretary Franklin Institute, 15 S. 7th St., Philadelphia, Pa.	Apr. 3, 1902
Wainwright, J. W., M.D.	177 W. 83rd St., New York.	Apr. 3, 1902
Waite, Loren G.	1381 Boston Road, New York.	July 3, 1902
Walker, C. R.	Consulting Chemical Engineer, 155 Western Ave., Cambridge, Mass.	Mar. 5, 1903
Walker, Dr. J. W.	Professor of Chemistry, Chemistry and Mining Building, McGill University, Montreal, Can.	Dec. 4, 1902
Walker, W. H., Ph.D.	Little & Walker, 19 Exchange Place, Boston, 613 Walnut St., Newtonville, Mass.	Aug. 7, 1902
Warmington, D. R.	Vice-President and General Manager, Peoples' Gas Light Company, 410 Pearl St., Cleveland, O.	Mar. 5, 1903
Waterman, Frank N.	150 Nassau St., New York.	Apr. 3, 1902
Weaver, W. D.	Editor, Electrical World and Engineer, 114 Liberty St., New York, Res. 55 Demarest Ave., Englewood, N. J.	Apr. 3, 1902
Webster, Edwin S.	Stone and Webster, 93 Federal St., Boston, Mass.	Apr. 3, 1902
Weedon, Wm. S., Ph.D.	Research Laboratory, General Electric Co., Schenectady, N. Y.	Apr. 3, 1902
Weil, Samuel	Superintendent, Electrical Lead Reduction Co., Niagara Falls, N. Y.	Oct. 2, 1902
Wells, Prof. J. S. C.	Columbia University, New York.	Apr. 3, 1902
Wells, J. Walter	Belleville, Ont., Can.	Apr. 3, 1902
Westman, Gustaf M.	1144 Broadway, New York.	Apr. 3, 1902

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		Date of election.*
Weston, Edward	Waverly Park, N. J.	Apr. 3, 1902
Wetzler, Joseph	President, The Electrical Engineer Institute of Correspondence Instruction, 240 W. 23rd St., Res. 257 W. 104th St., New York.	Jan. 8, 1903
White, Ray Hill, A.B.	170 Buffalo Ave., Niagara Falls, N. Y.	Oct. 2, 1902
Whiting, Prof. S. E.	Instructor in Electrical Engineering, Harvard University, Res. 11 Ware St., Cambridge, Mass.	Apr. 3, 1902
Whitlock, E. H.	First Assistant Superintendent, National Carbon Co., Res. 47 Eastman St., Cleveland, O.	May 9, 1903
Whitney, C. E.	Electrical and Mechanical Engineer, 123 Liberty St., New York, Res. 553 S. 6th Ave., Mount Vernon, N. Y.	Apr. 3, 1902
Whitney, Willis R., Ph.D.	General Electric Co., Schenectady, N. Y., and Massachusetts Institute of Technology, Boston, Mass.	Apr. 3, 1902
Whitten, Wm. M.	Pittsburgh Reduction Co., Niagara Falls, N. Y.	Apr. 3, 1902
Wiechmann, F. G., Ph.D.	P. O. Box 79, Station W., Brooklyn, N. Y.	Apr. 3, 1902
Wilbert, M. I.,	German Hospital, Philadelphia, Pa.	Apr. 3, 1902
Wilder, Stuart	Sanderson & Porter, 31 Nassau St., Res. 215 E. 15th St., New York.	Apr. 3, 1902
Wiley, Dr. H. W.	Chief of Bureau of Chemistry, Department of Agriculture, Washington, D. C.	Jan. 8, 1903
Willyoung, Elmer G.	11 Frankfort St., New York.	Apr. 3, 1902
Wilson, Leonard	Stanley Electric Mfg. Co., Pittsfield, Mass., Assistant in Engineering Department.	Dec. 4, 1902
Witherspoon, R. A.	Superintendent, The Ampere Electro-Chemical Co., Res. 170 Buffalo Ave., Niagara Falls, N. Y.	Oct. 2, 1902
Witherspoon, T. A.	Examiner, U. S. Patent Office, Washington, D. C.	Apr. 3, 1902
Wolcott, Townsend	329 Clinton St., Brooklyn, N. Y.	Apr. 3, 1902
Wood, E. F.	Vice-President, International Nickel Co., P. O. Box 1325, 74 Broadway, New York.	Apr. 3, 1902

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		Date of election.*
Wood, Walter A.	Sawyer-Mann Electric Co., New York, Res. Hotel Irving, Gramercy Park.	Apr. 4, 1903
Young, W. D.	Electrical Engineer, B. & O. R. R. Co., Res. 309 Oakdale Road, Roland Park, Baltimore, Md.	Apr. 3, 1902
Zeller, Frank M.	Continental Mfg. Co., Old Stock Exchange, Philadelphia, Pa.	Apr. 3, 1902
Zimmerman, C. I.	214 Brooks St., Madison, Wis.	Feb. 5, 1903
Zimmerman, Jas. G.	Assistant in Electrochemical Laboratory, Res. 214 Brooks St., Madison, Wis.	Nov. 6, 1902

(Number of Members, May 9, 1903..... 510.)

OBITUARY.

C. T. Child, elected April 3, 1902; died June 21, 1902.

A. B. Howard, elected April 3, 1902; died August 30, 1902.

C. W. Kennedy, elected April 3, 1902; died September 1, 1902.

H. C. Kohl, elected April 3, 1902; died November 10, 1902.

A. T. Weightman, elected April 3, 1902; died February 3, 1903.

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(May 9, 1903.)

UNITED STATES.

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Oxmoor.—McKeown, W. W., Tennessee Coal and Iron Co.

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Mayer.—Haggott, Ernest A.

ARKANSAS.

Fayetteville.—Gladson, Prof. W. N., University of Arkansas.

CALIFORNIA.

Los Catos.—F. Warren Smith, California Powder Works.
Martinez.—Peyton, W. C.
Sacramento.—Lichthardt, G., 1800 M St.
San Francisco.—
Allen, Wyatt H., 331 Pine St.
Arden, Henry, 900 Pine St.
Emery, Arthur L., Indiana and 24th Sts.
Hunt, A. M., 331 Pine St.
Lee, F. V. T., 31 and 33 Montgomery St.
Molera, E. J., 606 Clay St.
Vander Naillen, Prof. A., 113 Fulton St.
Wagner, Dr. Henry L., 522 Sutter St.

COLORADO.

Argo.—Fritchle, Oliver P.
Aspen.—Doolittle, C. E.
Denver.—
Frenzel, Arthur Benjamin, 1540 Sherman Ave.
Lacey, F. H., Colorado Iron Works Co.
Leadville.—Kyle, T. D., 106 E. 5th St.
Ouray.—Laughlin, W. C.

CONNECTICUT.

Hartford.—Johnson, Woolsey McA., 69 Vernon St.
New Haven.—
Bradley, Walter M., 1346 Chapel St.
South Norwalk.—Powell, Thomas H.
Windsor.—
Eddy, A. H., Eddy Electric Manufacturing Co.
Heath, H. E., Eddy Electric Manufacturing Co.

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DELAWARE.

Wilmington.—Krebs, A. S., Krebs Pigment and Chemical Co.

DISTRICT OF COLUMBIA.

Byrnes, Eugene A., 918 F. St., N. W.
Ewin, James L., 900 F St., N. W.
Frazier, Robert T., 918 F St.
Hopkins, N. M., 1730 I St., N. W.
Lloyd, M. G., Nat. Bureau of Standards.
Marvin, A. B., Jr., Patent Office.
Reber, Samuel, Headquarters of the Army.
Snelling, O. W., 3412 13th St., N. W.
Townsend, C. P., 918 F St., N. W.
Wiley, H. W., Chief of Bureau of Chemistry, Dept. of Agriculture.
Witherspoon, T. A., Examiner, U. S. Patent Office.

GEORGIA.

Savannah.—
Meldrum, Archibald, Box 144.
Nunn, Dr. Richard J., 5 York St., East.
Taylor, M. Temple.

ILLINOIS.

Chicago.—
Askew, C. B., 1652 Monadnock Building.
Bates, Wm. S., 510 Boylston Building.
Brill, Geo. M., 1134 Marquette Building.
Freeman, C. E., Armour Institute.
Hall, Jos. B., General Electric Co.
Hoskins, Wm., 81 S. Clark St.
Knapp, Geo. O., 157 Michigan Ave.
Lansingh, V. R., 18 E. Adams St.
Long, Frederic H., 84 Adams St.
Lyman, Jas., Monadnock Building.
Morehead, J. M., 157 Michigan Ave.
Rochlitz, Prof. Oscar A., Armour Institute.

Urbana.—
Brooks, Prof. Morgan, University of Illinois.
Lincoln, A. T., University of Ill.

INDIANA.

Bloomington.—Brown, Prof. Oliver W., Indiana University.
East Chicago.—Doggett, Chas. S., Grasselli Chemical Co.
Geneva.—MacFadden, C. K.
Indianapolis.—Hadley, A. N., Box 33.

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Lafayette.—
Ferry, Prof. E. S., Purdue University.
Goldsborough, Prof. W. E.

KANSAS.

Argentine.—Hofmann, Ottokar, Southwest Chemical Co.

KENTUCKY.

Danville.—
Gordon, Prof. Clarence McC., Central University of Kentucky.
Palmer, Prof. Chase, Central University of Kentucky.

LOUISIANA.

New Orleans.—
Johnson, F. C., 714 Union St.
Porter, John L., Laboratory of Sewerage and Water Board.

MAINE.

Cumberland Mills.—Gabriel, George A., Box 390.
Great Works.—Larchar, Arthur B., Penobscot Chemical Fibre Co.
Lewiston.—Robinson, Almon, P. O. Box 54.
Orono.—Burbank, Prof. John E., University of Maine.

MARYLAND.

Baltimore.—
Keller, Edward, P. O. Box 724.
Knorr, Aug. E., Baltimore Copper Smelting and Rolling Co.
Parsons, Louis A., Johns Hopkins University.
Smith, E. A. C., Baltimore Copper Smelting and Rolling Co.
Young, W. D., Baltimore & Ohio Railroad Co.

MASSACHUSETTS.

Amherst.—Howard, Prof. S. F., Massachusetts Agricultural College.
Boston.—
Amster, N. L., 32 Equitable Building.
Bleecker, John S., 93 Federal St.
Buchanan, Leonard B., 93 Federal St.
Cabot, Godfrey L., 82 Water St.
Cates, Louis S., 18 Post-Office Sq.
Goddard, Chris. M., 55 Kilby St.
Goodwin, Dr. H. M., Massachusetts Institute of Technology.
Pickering, O. W., Massachusetts Institute of Technology.
Pratt, Frederick S., 93 Federal St.
Rollins, Wm., 250 Marlborough St.
Schlesinger, Barthold E., 92 Mount Vernon St.
Stone, Chas. A., 93 Federal St.
Sweet, H. N., 50 Beacon St.
Walker, Wm. H., 19 Exchange Place.
Webster, Edwin S., 93 Federal St.
Whitney, Dr. Willis R., Massachusetts Institute of Technology.

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Brookline.—Howard, Henry, 175 Mountfort St.
Cambridge.—
Adams, Prof. C. A., Harvard University.
Adams, Isaac, 1776 Massachusetts Ave.
Kennelly, Arthur E., Harvard University.
Leavitt, E. D., 2 Central Square.
Walker, C. R., 155 Western Ave.
Whiting, Prof. S. E., 11 Ware St.
Concord.—Smith, Wm. Lincoln.
Dedham.—Coggeshall, G. W., Chestnut St.
Lawrence.—Alden, John.
Lynn.—Fleming, R., General Electric Co.
Newton Center.—Melcher, Arthur C., 58 Bowen St.
Pittsfield.—
Creighton, Elmer E. Farmer, Stanley Electric Manufacturing Co.
Kelley, John F., Stanley Electric Manufacturing Co.
Rushmore, David B., Stanley Electric Mfg. Co.
Wilson, Leonard, Stanley Electric Mfg. Co.
Quincy.—Clare, Jas. P., 51 Edison St.
Wakefield.—Skinner, Hervey J., 15 Chestnut St.
Worcester.—
Higgins, Aldus C., Norton Emery Wheel Co.
Jeppson, Geo. N., Norton Emery Wheel Co.

MICHIGAN.

Ann Arbor.—
Bigelow, S. L., 1520 Hill St.
Carhart, Prof. H. S., University of Michigan.
Patterson, Geo. W., Jr., University of Michigan.
Detroit.—
Barnes, S. G., 310 Boulevard West.
Herbert, C. G., 303 Hubbard Ave.
Shattuck, A. F., The Solvay Process Co.
Midland.—
Dow, Herbert H.
Shepherd, Lee, Dow Chemical Co.
Sault Ste. Marie.—Edmands, I. R., Union Carbide Co.

MINNESOTA.

Minneapolis.—
Frankforter, Prof. G. B., University of Minnesota.
Smith, S. N., 725 Temple Court.

MISSOURI.

Columbia.—
Brown, Prof. W. G., University of Missouri.
Shaw, Prof. H. B., University of Missouri.
St. Louis.—
Anderson, Edward L., 2700 Euclid Ave.
Goldsborough, W. E., World's Fair.

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MONTANA.

Anaconda.—Magnus, Benjamin.
Helena.—Gerry, M. H., Jr., Missouri River Power Co.

NEBRASKA.

Lincoln.—Evans, Herbert S., University of Nebraska.

NEVADA.

Virginia City.—Ross, G. McM.

NEW HAMPSHIRE.

Berlin.—
Barker, E. R., Burgess Sulphite Fibre Co.
Barton, Chas. B., Burgess Sulphite Fibre Co.
Nakayama, T., Burgess Sulphite Fibre Co.
Concord.—Coit, Dr. James Milnor, St. Paul's School.

NEW JERSEY.

Bayonne.—Backus, H. M., 47 Avenue C.
Camden.—
Norman, Geo. M., General Chemical Co.
Robbins, W. A., 535 Bailey St.
East Orange.—
Aylsworth, J. W., Edison Storage Battery Co.
Fliess, Robert A., 44 Chestnut St.
Elizabeth.—Granbery, J. H., 561 Walnut St.
Jersey City.—Stearns, Theron C., 47 Montgomery St.
Newark.—
Colby, Edward A., Baker Platinum Works.
Gifford, Wm. E., 59 Emmet St.
Rowand, L. G., Clover and Ferguson Sts.
Thowless, O. M., P. O. Box 273.
Van Winkle, A., 35 Lincoln Park.
New Brunswick.—Voorhees, Louis A., P. O. Box 357.
Nutley.—Thomas, Chas. W.
Orange.—Edison, Thomas A.
Perth Amboy.—
Addicks, Lawrence, Raritan Copper Works.
Easterbrooks, Frank D., Raritan Copper Works.
Foersterling, Dr. Hans, Roessler & Hasslacher Chemical Co.
McCoy, W. Asa, 57 Kearney Ave.
Princeton.—Loomis, Prof. E. H.
Rutherford.—Petty, Walter M.
Summit.—Speiden, Clement C.
Waverly Park.—Weston, Edward.
Woodbridge.—Doney, D. C.

NEW YORK.

Auburn.—Case, Willard E.
Brooklyn.—
Fletcher, Geo. W., 38 Grove St.

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Haslwanter, Chas., 908 Willoughby Ave.
Hutchinson, R. W., Jr., Polytechnic Institute.
Machalske, Dr. F. J., P. O. Box 25, Station W.
Main, Wm., 299 Jefferson Ave.
Sheldon, Dr. Samuel, Polytechnic Institute.
Wiechmann, F. G., P. O. Box 79, Station W.
Wolcott, Townsend, 329 Clinton St.

Buffalo.—

Bierbaum, C. H., Lumen Bearing Co.
Devine, Jos. P., National Battery Co.
Heckman, J. Conrad, Larkin Soap Manufacturing Co.
Moses, Herbert B., 366-382 Massachusetts Ave.
Perkins, Frank C., 126 Erie Co. Bank Building.

Clinton.—Saunders, Prof. A. P., Hamilton College, Clinton, N. Y.

Elmira.—Carrier, C. F., 511 Union Place.

Flatbush.—Barr, B. M., 234 E. 21st St., L. I.

Ithaca.—

Bancroft, Dr. Wilder D., Cornell University.
Carveth, Prof. Hector R., Cornell University.
Shepherd, E. S., 205 Hazen St.

Kingston.—Granja, Rafael, President Ceres Chemical Co.

Lansingburgh.—Kern, E. F., Betts' Laboratory.

Lockport.—

Davis, F. J., Cowles Electric Smelting and Aluminum Co.
Kenan, Wm. R., Jr.

Mount Vernon.—Blackmore, H. S., 206 S. 9th Ave.

New York.—

Adams, Ernest K., 455 Madison Ave.
Adams, Geoffrey C., New Amsterdam Hotel.
Allyn, R. S., 41 Park Row.
Atwood, Geo. F., Western Electric Co.
Austen, Dr. Peter T., 80 Broad St.
Banks, Wm. C., 439-445 E. 144th St.
Barstow, W. S., Bowling Green Offices.
Batchelor, Chas., 52 Broadway.
Benjamin, Dr. G. H., 20 W. 11th St.,
Block, Wesley S., 40 Wall St.
Bogue, Chas. J., 213-215 Center St.
Bowman, Walker, 39 Cortlandt St.
Bradley, Chas. S., 44 Broad St.
Brown, Harold P., 120-122 Liberty St.
Brown, J. Stanford, 489 Fifth Ave.
Browne, Wm. Hand, Jr., Park Row Building.
Caldwell, Edward, 114 Liberty St.
Cameron, Walter S., 239 W. 136th St.
Chandler, Dr. C. F., Columbia University.
Chasteney, C. D., 74 Cortlandt St.

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Coblentz, Dr. Virgil, New York College of Pharmacy.
Coho, H. B., 114 Liberty St.
Crocker, F. B., Columbia University.
Devlin, S. B., 156 W. 13th St.
Doremus, Dr. Charles A., 17 Lexington Ave.
Dreyfuss, W., 162 E. 95th St.
Drobegg, Dr. Gustave, 81 Maiden Lane.
Dunn, Clifford E., 13-21 Park Row.
Durant, Edward, 115 E. 26th St.
Eimer, A., 205 3rd Ave.
Elliot, Arthur H., 4 Irving Place.
Falding, Frederick J., 52 Broadway.
FitzGibbon, R., 77 John St.
Forbes, Francis, 34 Nassau St.
Frasch, Hans A., 52 Broadway.
Hanchett, Geo. T., 116 Liberty St.
Hatzel, J. C., 114 5th Ave.
Havemeyer, H. O., Jr., 117 Wall St.
Herzog, F. B., 51 W. 24th St.
Howe, Henry M., Columbia University.
Isakovics, Alois von, 449 E. 121st St.
Jenks, W. J., 120 Broadway.
Johnston, Thomas J., 11 Pine St.
Keith, N. S., 95 Liberty St.
Kennedy, J. J., 52 Broadway.
Kenyon, Wm. H., 49 Wall St.
Kintner, C. J., 45 Broadway.
Klipstein, Ernest C., 122 Pearl St., P. O. Box 2833.
Knudson, A. A., 34 Nassau St.
Langton, John, 99 John St.
Levine, Edmund J., 636-8 Broadway.
Lockwood, Chas. E., 439 E. 144th St.
Loeb, Morris, 37 E. 38th St.
Lyndon, Lamar, Park Row Building.
Mailloux, C. O., 76 William St.
Maynard, Geo. W., 20 Nassau St.
Maywald, F. J., 80 Broad St.
McKittrick, F. J. A., General Electric Co.
McNeill, Ralph, 510 W. 23rd St.
Metz, H. A., 122 Hudson St.
Monell, A., 74 Broadway.
Morehead, J. T., 99 Cedar St.
Morgan, J. L. R., Columbia University.
Morrison, W. J., Jr., 60-62 Broadway.
Mullin, E. H., 44 Broad St.
Nadolsky, Wm. L., 110 Chrystie St.

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Osterberg, Max, 11 Broadway.
Paget, Dr. L., 80 Greenwich St.
Park, Edgar, Hanover Bank Bldg., 5-7 Nassau St.
Pattison, Frank A., 141 Broadway.
Poole, Cecil P., 114 Liberty St.
Poole, Herman, 157 W. 106th St.
Potter, Henry Noel, 510 W. 23rd St.
Recklinghausen, Dr. Max von, 11 E. 24th St.
Reynolds, F. G., 368 St. Nicholas Ave.
Ries, Elias E., 116 Nassau St.
Riker, John J., 46 Cedar St.
Roberts, I. L., 40 Wall St.
Roller, F. W., 203 Broadway.
Rossi, A. J., 35 Broadway.
Schlegel, John W., 602 E. 5th St.
Schreiter, Henry, 20 Nassau St.
Seeger, L., 52 Broadway.
Seward, Geo. F., 97 Cedar St.
Stein, Emanuel, 45 Broadway.
Teala, N., 46 and 48 E. Houston St.
Thelberg, Dr. John, 45 W. 32nd St.
Thompson, Robert M., 74 Broadway.
Volney, C. W., 173 W. 81st St.
Wainwright, Dr. J. W., 177 W. 83rd St.
Waite, L. G., 1381 Boston Road.
Waterman, Frank N., 150 Nassau St.
Weaver, W. D., 114 Liberty St.
Wells, Dr. James S. C., Columbia University.
Westman, Gustaf M., 1144 Broadway.
Wetzler, Joseph, 240 W. 23rd St.
Whitney, C. E., 123 Liberty St.
Wilder, Stuart, 31 Nassau St.
Willyoung, Elmer G., 11 Frankfort St.
Wood, E. F., P. O. Box 1325, 74 Broadway, New York.
Wood, Walter A., Sawyer-Mann Electric Co.

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Presidential address delivered at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, Vice-President Doremus in the Chair.

CONDITIONS OF PROGRESS IN ELECTROCHEMISTRY.

By Joseph W. Richards, M.A., A.C., Ph.D.

To live is to progress, and to progress is to live. A science which does not progress, petrifies. As the progress of electrochemistry is, however, only one phase of scientific progress in its more general sense, a clear understanding of the laws governing the latter will teach us, as their corollaries, the conditions for progress in the former.

Science advances in many different ways, along many different paths and by many different agencies. For the purpose of our discussion this evening, I will classify this progress under six headings, as follows:

1. Discovery of new facts.
2. Clearer understanding of the laws correlating facts.
3. More rational theories of the why and wherefore.
4. Increasing application of the facts to the welfare of mankind.
5. Increasing dissemination of scientific literature.
6. An increasing vision, on the part of the scientist, of the possibilities of scientific achievement.

Other items than these six may suggest themselves as fundamental, but I believe they are all included in the above classification. Enthusiasm on the part of the scientist might, for instance, be cited as a very necessary condition for scientific progress, but in the last analysis this is seen to be a corollary of our item six: Increasing vision of the possibilities of scientific achievement is the all-sufficient generator of real enthusiasm in the worker.

The science of electrochemistry has progressed so magnificently in the last decade that a mere catalogue of its achievements would be a monumental compilation. Abler and better-informed pens than mine have given to us recently, in presidential addresses and in careful reviews, the detailed history of this progress. I do not intend to attempt that task anew this evening; my theme is an

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analysis of the *conditions which make for progress,* and which I hope to make clear in all their bearings on electrochemical science.

I. DISCOVERY OF NEW FACTS IN ELECTROCHEMICAL SCIENCE.

I place this as the corner-stone of progress in our science. Given a freshly-flowing current of new electrochemical facts, and all the other elements of progress have a chance to exist. No less certain than this, is the location of the birthplace and the identity of the sponsors of these newly-born facts. The birthplaces are chemical, electrical and physical laboratories; the sponsors are the investigators, the searchers after truth,—the professors, students, employees, private investigators, and all who with the insatiable thirst for more knowledge are pushing back the thick curtain of the unknown which hems us in so closely on every side. The elect among these workers, the highly-favored few, are the professors of electrochemistry provided with well-equipped electrochemical laboratories. They are in the position to do or to direct the most valuable investigations, and are also under the moral obligation to publish freely to the world all that they discover. The giants of the electrochemical fraternity are in this class: Davy, Faraday, Bunsen, Arrhenius, van't Hoff, Ostwald, Nernst, Moissan. The labors of such workers, given to the world in their publications, form the *body* of electrochemical science, and their thoughts—its *soul.* Such are the heroes of science; men who work for the work's sake, who sacrifice time, money, and often health, to increase the boundaries of our knowledge, and then keep nothing back. These are the sort of men whose grateful memory we should perpetuate in bronze and marble, as well as in our literature. Great wealth has been amassed by the application of the facts discovered by these pioneers, and yet the facts are at the command of any one who will read our literature. And there are others of the rank and file following cheerfully the same paths; our journals and transactions teem with the results of new researches, by which the humble worker in one corner of the scientific field gains the knowledge gleaned by many workers, and in return he contributes what he can, and every such contributor, mark it well, receives in return a hundredfold for all that he himself contributes.

The German-speaking countries count up alone at their univer-

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sities and technical schools 15 chairs of electrochemistry and 12 electrochemical laboratories. These, we all know it, have been the source of the greater part of the advance of electrochemical science in the last ten years. The whole industrial electrochemical world is debtor to the European electrochemical laboratories and their workers, and how can that debt be requited? Surely not by selfishly using all the facts and holding fast all the material benefits. Not only common gratitude but also self-interest unites in recommending to the captains of electrochemical industry that more such laboratories be built and more such chairs endowed; money thus spent will be seed which will return many fold its value to the industry. America has boasted that it is "The Electrochemical Centre of the World." It may be so, in the development of electrochemical industries, in the amount of power used and material products turned out; but is it not a fair question to ask "Where are the professors of electrochemistry at our universities and how many electrochemical laboratories are at their command?" Are we not out of comparison with Germany in that respect,—but I trust not hopelessly so? Our present flourishing condition industrially is largely due to our foreign-trained electrochemists and our imported literature. Shall we not, through shame at contributing so little ourselves to that literature, soon begin to establish chairs of electrochemistry and build well-equipped laboratories to go with them? Then our boast might begin to be more than the empty boast of a successful money-maker; then we may begin to be an *illuminating* centre radiating knowledge to the rest of the world.

In place of professors and professional laboratories, however, America is blessed with another class of investigators who are no less industrious in acquiring facts, and to whom a large part of our commercial success is directly ascribable: I refer to the small army of patient investigators in the laboratories of our industrial plants, who are searching over ground not yet explored and accumulating facts of value in their special industrial lines. The expense of such work is borne by the corporation for which they labor, and the work itself is in reality an investment made in the hope of yielding financial reward. Such workers frequently discover important facts, and are also frequently importuned by well-meaning editors and "committees on papers" to publish their re-

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sults to the world and thus add to the body of observed facts known to science. But such importunity, whenever it passes the bounds of mere request or encouragement to publish, is very much out of place; it is bad taste. The workers in industrial laboratories are, by the nature of the case, not at liberty to publish what they discover; the monetary fruits of their work are the property of their employers, or of the stockholders of their corporation, and it is the plain duty of said investigators to preserve their trust faithfully and to publish their results only when they have full permission to do so.

And yet, the fact that such requests are so frequently made is an indication that electrochemical science feels that it has some right of eminent domain to all discovered electrochemical truth. There is no conscientious worker who does not feel deeply the debt which he owes to the intellectual giants of the science, on whose shoulders he stands when making his researches, and the obligation to whom can only be properly requited by enlightening, in his turn, the path for those who follow him.

Where then do these two obligations which I have spoken of meet; the obligation to the employer and that to the science? There is one sufficient answer: *When the research has achieved its financial purpose, the scientific results should be given to the world.* In other words, when the laboratory experiments have led up to the technical process, and the latter has been protected by patents, then the scientific principles discovered during the investigation should be freely published. To pigeon-hole them longer than is necessary to make sure the financial side of the process discovered, is base ingratitude towards the *alma mater* which made such researches possible. As to the *when* and the *how,* as well as the *extent* of such publication, the investigator in conjunction with his employer are the proper judges of the question, and the matter must in the nature of the case, be left to their discretion. If they appreciate as they should the debt which they owe to the science as a whole, they can safely be trusted with deciding the question honestly and fairly to all interested and concerned.

II. CLEARER KNOWLEDGE OF THE LAWS CORRELATING THESE FACTS.

By means of facts, correlating, discussing and deducing therefrom, we arrive at a knowledge of the laws of the science, the

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rules governing its various phenomena and according to which its manifestations invariably proceed. Such deductions are the goal of pure science; they contain no element of speculation, hypothesis or theory, and represent man's deepest insight into the phenomena of nature.

The indefatigable Faraday discovered our first fundamental laws. Ohm and Joule added to them, and numerous later investigators have contributed, but we must not make the mistake of thinking that there remains very little more in the nature of generalizations to be discovered; we could not make a greater mistake. If facts are being discovered, the recognition of unforeseen generalizations and the establishing of new laws is bound to follow, and thus the science reaches its highest consummation.

Such discoveries are usually the privileges and the perquisites of the experimenter and investigator, if so be that he is likewise a thinker. He gets the facts at first hand, and has the first chance to deduce new laws. The electrochemist not blessed with laboratory facilities has, however, free entrance to this field. He may be only a student, a looker-on at what others are doing, a reader of the newly discovered and recorded facts, but if he is at the same time a thinker, a compiler, an analyst with the power of collating, dissecting and deducing, he may in the seclusion of his study discover laws which escape the observation of others less studious, and thus render a service of the highest value to the science.

The progress of science thus requisitions and makes place for all orders of ability in its service, and some of its greatest achievements are to be won by the electrochemist who, although destitute of a laboratory, nevertheless keeps himself well-informed, is blessed with diligence in study and a clear head for inductive reasoning. Such a one may be privileged to discover some of the most fundamental laws of our science.

III. MORE RATIONAL THEORIES OF THE WHY AND WHEREFORE.

As soon as facts accumulate and laws are discerned, the scientist inevitably begins to reflect on the why and the wherefore. He commences to search for relations, to imagine connections and dependencies, and to make pictures of the mechanism of the phenomena. It was thus that Dalton imagined the atomic theory to account for the fact of chemical combination in simple multiple

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proportions, that Arrhenius hit upon the dissociation theory to account for the increase of molecular conductivity with increasing dilution, that Nernst worked out the solution-pressure theory to explain the generation of current in the galvanic cell. Thus there are theories and theories, some poor, some good, and some almost perfect in their applicability, since, *granting their premises,* they give an explanation satisfactory to the mind, of all observed phenomena.

Such theories are not only allowable, but necessary. We must have them, much as an artisan must have a working drawing of the machine he will construct; the drawing is but paper and ink, which never moves or works, but it guides the workman in putting his ideas into realities. So theories help us to handle mental conceptions as if they were concrete things, and thus to imagine and discover relations and generalizations which would otherwise be beyond our mental grasp.

The danger to the development of a science comes when a theory, by being believed too implicitly and by not being open to constant revision, becomes a straight-jacket for the growing science. Like a "creed outworn," it stifles criticism, warps the judgment, engenders blindness and bias in its adherents and undue hostility and acrimony in its opposers. We should be slow in revising our theories, or in discrediting a theory which has done us good service in its day, just as we are conservative in correcting our "confessions of faith" or indulgent and sympathetic with the weaknesses of a faithful old servant; but, after all, when a theory has come to be considered so firmly fixed as to be above criticism, or so certainly true as to be above the possibility of revision, or so well-established as to thunder its excommunications on those who dare to think or believe otherwise,—such a theory had better be placed at once in the museum of scientific petrifactions, where it properly belongs and where it can do no further harm.

If science is progressing, theories must progress too; they will be outgrown, much light will give way to more light, imperfect pictures of phenomena founded on crude assumptions must be replaced by better pictures corresponding more accurately to the newer and the larger truth, and then progress begins anew.

All theories have been of some use in their day; they have helped men to grasp concretely evanescent immaterial phenomena,

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they have very often been splendid guides to further experiment and new discoveries, they have at times been so helpful that many have mistakenly thought them infallible, and lastly, they have been stepping-stones to better theories. One great hindrance to scientific progress is the common human weakness of becoming partisans of a theory. Who is not familiar with the well-meaning theorizer whose mental vision is so biased that he refuses or is incompetent to give a fair reception to new facts and theories; or who has not met the egotistical speculator who experiments and makes researches not to discover truth but to prove his pet theory? It might be thought that it makes no difference what the motive, so long as the work is performed, but it does make a world of difference. The biased investigator, with a theory to support, is apt to support it at all hazards, he catches at every straw which helps to establish his preconceived idea of what he should find, and is virtually blind to facts which disprove his ideas, while his report of his work, filtering through his perverted imagination, gives as often as not an entirely distorted picture of the facts. The scientific world, having to content itself with this report, shares to that extent the mental strabismus of the investigator. The pitfall is particularly dangerous to the young and ardent investigator. Believing almost implicitly in the rectitude and ability of his instructor, he takes to his professor's hobby with enthusiasm, and spurs it on to feats which make more careful scientists shudder. He rattles off glibly the shibboleth of the pet theory, talks of its hypotheses as if they were facts proved beyond all question, smiles superciliously at any one who questions the accuracy of his statements, and often gets irritated at the most friendly and unavoidable criticism. Thus the warmest friends of a theory are often its worst enemies, and by their blind partisanship lay obstacles in the path of scientific progress instead of being the leaders which they might be.

To make a specific application of these remarks, who has not felt that the most effective blows dealt the present theory of electrolytic dissociation have come from the excessive zeal of its warmest adherents? Out of their camp has proceeded half-fledged treatises on the theory, such as inaugural dissertations of would-be doctors of philosophy or text-books compiled by privat-docents, in which the theory was simply done to death and made a laughing

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stock. Have we not met writers or lecturers on this theory who shunned a fair debate on their written or spoken statements, because, forsooth, they were themselves conscious that they had surpassed the safe bounds of reasonableness in those statements? Such an attitude, and such results are the consequence of holding a theory too tenaciously, and not "subject to revision." There are scientific zealots as well as religious bigots, and the one does as much harm to the progress of true science as the other does to the development of pure religion.

The fundamental conceptions of any and every theory must always be open to correction and revision, and thus progress will be rendered easy. If new facts appear which contradict our theories, let us welcome them, like loyal lovers of the truth should. The theory of electrolytic dissociation is being saved by being modified and revised, it is being transformed into a more perfect mirror of the truth as we now conceive it, and thus only is it retaining its usefulness and aiding in scientific progress.

IV. INCREASING APPLICATION TO INDUSTRIAL NEEDS.

In order not to become a mere code of observed and classified facts, a thing to interest men by its intrinsic perfection but of no other earthly use, a science must find practical applications which increase the comfort, pleasure or wealth of mankind. In this field, electrochemistry is in no manner lacking, it abounds in notable achievements. If that man is a benefactor of the race who figuratively makes two blades of grass to grow where but one grew before, then the practical electrochemist certainly takes high rank among the benefactors of mankind. The whole circle of human industry consists in utilizing the fleeting value of the perishable capacity to labor, linking it with natural forces and thus turning into valuable products natural crude material. The items concerned are crude material, power, brains and industry.

Power alone is apt to be regarded as the first desideratum for the success of electrochemical processes, but knowledge, thinking power and industry are more primary factors. Given these, crude materials to work with will be found on every hand, and power sufficient will be created if it is not to be found.

A few words, however, about this question of the necessary cheap power. This item in manufacturing cost is of variable im-

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portance in electrochemical processes; in some it may form three-quarters of the total cost of the process, in others perhaps only one-quarter. The former are frequently compelled to move to the cheapest power, in order to exist at all, while such as the latter may take into account many other considerations, and find it cheaper for them to locate at more expensive powers. Niagara Falls is the most accessible of our great water powers, and has therefore drawn into its fold the majority of our electrochemical industries. But another source of surplus power is distributed over a large part of our country, in a condition at present as undeveloped as was Niagara power when Columbus touched our shores. I refer to the surplus power from blast-furnaces, obtainable by using gas-engines. Every blast-furnace burns its gases to heat its blast and to raise steam for its power. The two-thirds of its gases used for the latter purpose generate just about the power needed for the blowing-engines, pumps, hoists, etc., an amount equal on an average to 2500 horse-power for a furnace making 500 tons of iron per day. If the gas thus used was used in gas-engines, there would be an average surplus power, over and above all the requirements of the furnace itself, of 10,000 horse-power. The gas-engine plant needed to produce this power does not cost over $50 per horse-power investment, which compares favorably with the cost of developing water-powers, which vary from $25 to $100 per horse-power. It is thus deducible, that there are scattered over the United States, in some of our most flourishing industrial centres, undeveloped powers which aggregate over 1,000,000 horse-power, which can be developed at no more cost than the average water-power, can be generated just at the spots where they can be most favorably utilized, and without any more drain on our natural resources than the harnessing of a new water-power,—for not a pound of coal more would have to be burnt than is used at present.

Other possible sources of power are the waste surplus gases from by-product coking ovens, and the utilization of gas-producers, using cheap, almost waste, coal, in connection with gas-engines. Power therefore is available in immense quantities in places and in countries not blessed with Niagaras in their midst, and the industrial development of such sources will be one of the most marked industrial movements of the next ten years.

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And now, let us inquire, how is this increasing development of power and its increasing application to industrial purposes best promoted by the electrochemists themselves? Undoubtedly, it is by the intimate and cordial co-operation of theoretical with practical electrochemists. This is attained by many agencies, but the most potent are Research Companies and our Electrochemical Society.

Such organizations as Research Companies, formed explicitly to combine research with practical application, are novelties in the industrial world which have originated with, and are almost peculiar to, electrochemistry. They invent, investigate and develop electrochemical process, and furnish facilities to would-be experimenters whose ideas might otherwise remain still-born. Such companies deserve the hearty support of all electrochemists, for they are injecting new life into the industry. May we have more such, scattered all over our land to nurse and develop quickly into active being the many electrochemical processes which *are to be.*

Our society conventions furnish the other most potent factor in stimulating industrial applications, for by bringing into personal relations theoretical and practical workers, who there freely interchange thoughts, experiences and ideas, the sum total of possible progress thus engendered is entirely beyond our power to calculate or express. We do not attempt to estimate it concretely, but content ourselves with feeling the absolute certainty of its results. The meeting of electrochemists with practical chemists, as in our present assembly, or with electrical engineers, as at our gathering last night, also cannot be without its beneficent results in this same direction.

The factors which promote increasing applications of electrochemistry are therefore cheap and accessible power, experimentation on a semi-industrial scale, men with heads full of ideas and inventiveness in applying them to the industrial needs of the country, more research companies and a further cultivation of the beneficent results of our society meetings.

By thus doing, cheap raw materials will be converted by the electrochemist into valuable products with constantly increasing ease and constantly decreasing cost, and thus electrochemistry will achieve its great *raison d'être* by increasingly ministering to the

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needs, the comforts and the pleasures of life, and thus it will become an increasingly important factor in social progress.

V. AN INCREASING DISSEMINATION OF THE LITERATURE AND FACTS OF THE SCIENCE.

No modern science can progress if it adopts the medieval practice of the alchemists, and carefully guards its wisdom for the exclusive use of the initiated. Wide-spread dissemination of the literature of our science, not only among our own fraternity but among educated people in general, and even down to the rising generation of expectant scientists, is as necessary to our progress as is the recruiting of the human family to the preservation of the race.

The literature of our science consists of transactions, journals, treatises, monographs and text-books. Without these, and without the constant extension, improvement and dissemination of the same, our science would soon be dead indeed.

The transactions of our societies are the standing record of papers and discussions presented at our meetings. The contents represent the labors of many heads and hands, and the opinions of many minds. As such, they form a permanent record of the latest advances and the best thought in electrochemical lines. They are the reservoirs of information from which the other literature of the science, such as treatises and monographs, are largely compiled. They are of particular value to people who cannot personally attend the meetings which they report. Their value is augmented by being quickly printed and distributed, and the publication committees having that task in their charge should receive the co-operation of all authors in their efforts to prevent the transactions from becoming ancient history before they are issued. We may be pardoned referring with a little pride to the fact that the report of our Niagara meeting was distributed seven weeks from the close of the meeting, and that twenty-five per cent. of the papers presented at this, our most notable New York meeting, were in print before the meeting began.

The increasing membership of our societies, and the placing of such transactions in scientific and public libraries, are potent means towards interesting and instructing the world in electrochemistry, and recruiting the army of electrochemical workers.

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Our journals serve to keep us posted as to current events and as to what is being done by others outside of our immediate circles. Our journalism should be in the most able hands, for a capable editor can render service of the first importance to all his readers, by culling out and presenting to them only the best and the reliable, and fearlessly scoring the financial shark and the scientific impostor; while, on the other hand, an incompetent in the editorial chair can lower the tone of the literature of the science by giving standing to trash of all sorts which he may be either afraid to criticise or incompetent to pass proper judgment upon. A clean, upright, fearless, truth-telling journal, ably and conscientiously edited, deserves the support of every electrochemist, not only from the personal advantages thus gained but also from the beneficial effect which such a journal can and must have upon the progress of the science as a whole.

Monographs on applied and theoretical electrochemistry, and comprehensive treatises on the science, form the backbone of our literature. They sum up our information to date, on one or more, or on all topics, and so enable the specialist to become *au courant* with the present condition of any one branch of the field, or the general reader to get a comprehensive view of the whole of the science. The publication of such works should be encouraged in every way, when undertaken by competent hands, since the work is largely a labor of love. No scientific author receives more than day-laborer's wages for the time spent on his works. Moreover, since we have, unfortunately, no universal language, great service is done to the electrochemists of one country by translating into their language the best of what is published in foreign tongues. The great men of our science can scarcely do a single piece of work which will be of greater use, than to compile in a treatise or monograph their understanding of the present condition of the facts and theories of the science. Such books as Mendeléeff's "Chemistry," Arrhenius' "Theories of Electrolytic Dissociation," Nernst's "Theoretical Chemistry," Van't Hoff's "Vorlesungen," Moissan's "Le Four Electrique" serve to steady matters, they fix the attention and mould the thought of others not so well informed, and so give coherence and system to the progress of the science.

Our text-books, intended to give beginners their first ideas of

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electrochemistry, should be most carefully written. Nothing sticks so permanently in the mind as a correct idea taken in youth from a good text-book,—except an incorrect idea taken from a bad one, and I think that the latter often sticks the hardest. It used to be remarked that every professor elected to a chair of mineralogy in Europe felt himself expected to write a treatise on crystallography,—and he generally wrote it; it is, of course, an exaggeration to say that every privat-docent elected to lecture on electrochemistry writes a text-book on the elements of the science, but it is an exaggeration with a grain of truth in it. There are entirely too many imperfect or partisan or downright execrable text-books of this kind; one good one, written by a master, is worth more than all of these poor ones put together. Electrochemistry should also be better presented in the elementary text-books of chemistry and electricity. The inter-relation of these subjects is so intimate, that the fundamentals of either necessarily include some of the fundamentals of the other, and beginners are wonderfully apt at comprehending the essential fundamental facts if they are skilfully presented. I recall to mind a very complete modern text-book of inorganic chemistry, written by a splendidly-informed chemist, in which the electrochemical part was turned over to an assistant, and, as a consequence, abounds in mis-statements. We cannot afford to have our students started wrong, and it is therefore of the highest importance that our text-books, while being as brief as is necessary, be as accurate as is possible.

The newspapers frequently display semi-scientific articles written in popular style, dealing with such electrochemical matters as interest or amuse the public. If competent electrochemists were to write such articles they would do great service to the general public, by thus keeping out mistakes and exaggerations. The editors of our electrochemical journals are nearest to being in touch with the newspapers, and it is certain that reciprocal advantages would result from their cultivating closer relations with the daily press.

A living, active literature, supported by electrochemists in every legitimate way, is a *sine qua non* for the continued progress of our science, and I enlist in its behalf the active co-operation of one and all.

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VI. AN INCREASING VISION OF THE POSSIBILITIES OF THE SCIENCE.

If we ask the student of electrochemistry why he chooses this for his life-work, he will possibly reply that he has been advised, by counsellors in whose judgment he relies, that this is a most promising field for his activities; more probably he will answer that by reading himself some of the literature of electrochemistry he became attracted by the novelty of what was being achieved, and wished to take part in a science with such a promising future. In either case, the knowledge of what is and the vision of what may be, in this almost virgin field of human endeavor, is the magnet which draws recruits and adds to the working forces in our ranks.

If we ask the enthusiastic worker in his laboratory, what is the principal force keeping him at his work, which ever incites to fresh activity and lightens labors which might otherwise easily become tedious, the ready reply is that there is so much to do, so much to find out, so much promise of achieving great things, that he would be made of very dull stuff indeed who would not be enthused thereby. The ever-widening vision of an ever-widening field, is the reward and the inspiration of every honest worker, and is the mainspring of the mechanism whose working means progress to our science.

In every field of human endeavor, for the teacher in his classroom, the writer at his table, the editor at his desk, the workman at his labor, the investigator at his task, the chief incentive to happy, productive work is the vision and the promise of what may be attained. Without that vision, life would be dull indeed.

To the seers of old was ascribed the wisdom of the ages, and with the prophets they guided humanity to higher and nobler things. The see-ers saw before them and before humanity the things which might be, the promise of the future, the possibilities for development which lay before the race; they gave new life and hope to mankind by proclaiming the possibilities which might be achieved.

In like manner, each one of us is inspired and encouraged, nerved to high endeavor and imbued with the spirit to do and to achieve, by the sight or vision of the possibilities of electrochemical science. Some may have the vision but dimly, others see

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clearly and far into the future which yet lies so close before us, but each is privileged to share in part the vision of his neighbor.

If there is, therefore, one thing which an Electrochemical Society such as ours achieves of more superlative worth than any other thing, it is the resultant enlargement of vision which comes to each of its members, mainly and chiefly from the interchange of thought, the sharing of ideas, the communication of insights into the possibilities of the science, resulting from our semi-annual meetings. Does not each one of us go away from these meetings feeling that he has been sharing in the visions of all his electrochemical brethren, and with his mind often so overloaded with suggestions, thoughts and ideas of what may, can and will be done in the near future, that he wishes he had a dozen lifetimes at his command in order to work out to realization this plenitude of ideas? Such is the zeal and ardor which our meetings engender in a high degree, resulting from listening to papers and discussions, by conversations, by simple handshakes and seeing our friends, and by breathing the invigorating atmosphere of our assemblies.

Let us then, you and I, one and all, see it as our privilege as well as our duty to promote in every way the interest, the attractiveness and the scientific atmosphere of these meetings, for they are, if we will but realize it, the elixir of life to the development of electrochemistry in America.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

DETERMINATION OF VAPOR DENSITIES IN AN ELECTRIC FURANCE.

By Prof. Dr. W. Nernst.

The highest temperatures reached in vapor density determinations by Nilson and Petterson, V. Meyer and recently by Biltz[1] are between about 1700° and 1800°; the melting-point of the platinum or porcelain apparatus heretofore used was the limit which could not be overstepped.

As vapor density determinations are of great importance for the chemistry of high temperatures, and in view of the fact that, if the temperature is raised by a few hundred degrees, numerous substances become gaseous which have too low a vapor density at the temperatures at which heretofore measurements could be made, I have studied this problem for a number of years. After having made numerous unsuccessful experiments in this respect, I am now in a position to describe a method which enables relatively certain and exact measurements up to about 2000° and perhaps more.

(*1*) *Material of the Vessels.*—Experiments undertaken for the purpose of making gas-tight apparatus from mixtures of rare earths, have so far been without success. Yet I would not like to consider it as hopeless to make porcelain-like and at the same time extremely refractory vessels from such materials. But since the firm of Heraeus has recently succeeded in working iridium, which is well known to be very brittle, it has become possible to make apparatus which can stand temperatures of 2000° and more, its melting-point being about 2220°. The iridium must be welded into shape at a blinding-white heat.

(*2*) *Method of Measurement.*—The only possible method is Victor Meyer's method in which the displacement of air is measured. Of course, on one hand the difficulty of maintaining a larger vessel for some time constantly at about 2000°, and on the other

[1] Ztschr. phys. Chem., V, 385 (1896).

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hand, the high price of iridium, made it necessary to use apparatus of very small dimensions. The volume of the portion of the bulb which is at nearly uniform temperature was in the last experiments about 2.5 cc. and therefore the volume of the vaporized substance ought not to be much more than 1 cc. At the ordinary temperature of the room, the expelled air volume was then only about 0.13 cc., which had to be determined very accurately. This could be done in a very simple way by measuring the motion of a mercury meniscus in a calibrated capillary glass tube, acted upon by the air expelled from the iridium vessel.

Of course, very small quantities of material, often only portions of a milligram, were vaporized. The ordinary balances were therefore not sufficiently delicate, and I had to devise for my purposes an extraordinarily sensitive balance. As in the weighing an exactness of part of 1 per cent. is more than sufficient, the solution of this problem was relatively simple; I constructed by means of a thin glass thread a balance which acts according to the principle of an ordinary letter balance. Instead of an edge, I used a quartz fibre fastened to the suitably bent glass thread and held by a fork-shaped brass frame, *i. e.*, I applied the principle of a torsion balance. The glass thread ended in a pointer which moved over a glass scale divided into divisions of 0.5 mm.; the readings were taken with a telescope. This simple apparatus proved to be excellent. As it has been found to be suitable also for chemical analysis (atomic weight determinations) with very small quantities of substance, it will be described in detail at another place. It may be mentioned here only that at the start of the definite tests, one portion of the scale (0.5 mm.) corresponded to 0.0378 mg., and after the tests to 0.0380 mg.; by several repetitions of the weighing the accurateness could be easily increased to 0.001 or 0.002 mg. The calibration of the scale was made by means of an accurately weighed thin platinum wire which was cut into a number of approximately equal parts of about 1 mg. weight.

(3) *Heating Device.*—By means of a large oxy-hydrogen flame the required high temperatures could be easily obtained, but it would be more difficult to maintain them constant. However, the loud noise of such a flame renders its use very obnoxious; a well-adjustable electric heating device is certainly preferable. At first I tried to use resistance furnaces of tube form and made of suit-

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able refractory conductors of the second class (electrolytic conductors) which however were finally found to be less suitable for my present purpose. Iridium tubes proved to be excellent, heated by means of low tension alternating current; they are made by the firm of Heraeus with great perfection.

(4) *Temperature Measurement.*[1]—This was made by a photometric method. Below the vertical iridium furnace there was an electrolytic incandescent filament which had been calibrated by the photometer for various current strengths. By adjusting, with the aid of colored glasses, the brightness of the filament equal to that of the iridium vessel, and by measuring the corresponding current in the filament, the emission E of light from the iridium bulb per square millimeter could be directly found. Further, as the latter was in the iridium tube of equal temperature, the laws of radiation from a "black body" could be assumed as valid; whether the filament really radiates as a "black body" or not, is of no account.

In the following, the values of the temperatures, calculated from the emission of light according to Lummer and Trinysheim,[2] are given in centigrade degrees at the side of E in parenthesis. Besides, as is well known, the temperature does not enter into the calculation of the molecular weight by V. Meyer's method. The calculation of the temperature is at present only approximate but will become relatively exact, as soon as we get further results on the optical brightness as a function of the temperature. In the following, from the value of 0.5 Hefner candle per square centimeter at 1690°, the temperatures have been calculated under the assumption that the brightness increases with the 14th power of the temperature.[3]

(5) *Description of the Final Apparatus.*—All details will become clear from the accompanying diagram. The furnace is a tube of iridium 17.5 cm. long by 2 cm. in diameter, with platinum flanges F on the ends 4 cm. wide, serving for fastening the copper connections C. The walls are 0.5 mm. thick. A current of 300 to 400 amperes is passed through the tube, using 2 to 3 volts

[1] The method here described, which I have used for some time, is in principle the same as that of the optical pyrometer, described in the meanwhile by Holborn and Kurlbaum (Berl. Acad. Ber. 1901, p. 712); for such high temperatures it becomes especially simple and accurate, by the use of electrolytic incandescent filaments.

[2] Compare Rothmund, Nachrichten Math-phys. Klasse, Goettingen, 1901, Heft 3.

[3] See Lummer: Elektrotechnische Zeitschrift, **23**, p. 812 (1902).

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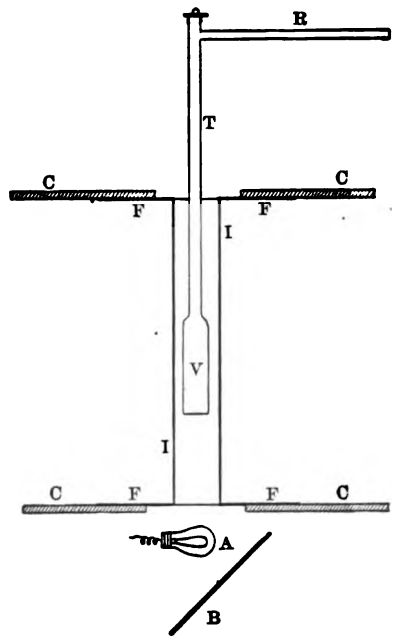
across the terminals, and the furnace may be thus heated up to 2200°. Strong copper conductors lead to the furnace, supplying it with about 2000 to 3000 watts from the thick wire (low tension) winding of an oil-cooled transformer. For heat protection, the iridium tube was surrounded with burned magnesia and this with a cover of asbestos. At the bottom the iridium tube was open so that by means of a small mirror, placed below the incandescent



filament, the radiation of the latter could be easily compared with that of the iridium vessel.

Iridium Vessel.—In the first experiments a vessel similar in form to a test-tube was used, which was closed at the top with platinum; to give to the inside volume the form of a pear, a magnesia tube was inserted into the upper part. With this apparatus, tolerably satisfactory figures were obtained. Dr. Riesenfeld, who has made these measurements, will give an account of the same at another place. A few months ago, however, I was surprised to receive a real iridium bulb from the firm of Heraeus, which has

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been heartily and actively interested in my work; it is a work of art of the first class and was put at my dispostion with the greatest liberality by the firm of Heraeus; it has been used throughout in the experiments which are here described.

This iridium tube consists of a thin tube T, 15 cm. long by 0.5 cm. internal diameter, terminating in a bulb V, 5 cm. long by 1 cm. diameter.

To the bulb, the upper capillary part of which was cooled by means of a copper tube through which water was flowing, there was connected by means of rubber the charging device R, which was made of brass in the well-known manner. The glass capillary tube which served for measuring the volume of expelled air was also connected by means of rubber in an air-tight manner. A suitable quantity of material was placed in small iridium buckets, as shown in the illustration, and placed in the charging device before the experiment. After each experiment, without changing anything else, the iridium vessel was ventilated by means of a platinum capillary tube, so that, in general, three or four experiments could be made quickly one after the other.

RESULTS OF THE EXPERIMENTS.

(1) *Carbonic Acid.*—As a substance for testing the apparatus, I used carbonic acid which was evolved in exactly known quantity by the introduction of a weighed piece of calcite. As long as there is an excess of oxygen present, there is no perceptible dissociation at the temperatures of the experiments. In the following tables n is the reading of the scale, g the vaporized quantity of substance, in milligrams, which is obtained in this case by multiplying quantity of calcite used by 0.4396.

As the value of a part of the scale (about 0.5 cm. long and divided into five subdivisions) is 0.0215 cc., the molecular weight of the vaporized substance for a reading of n parts of the scale is

$$M = 28.88 \frac{(1+\alpha t)\,760}{0.001293 \times 0.0215\,B} \frac{g}{n};$$

the temperature t of the glass capillary tube was 15° in the following test, the barometer reading B = 751 mm.; then, if we give g in milligrams instead of grams,

$$M = 1109 \frac{g}{n}.$$

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g.	n.	M.
0.3011	7.58	44.1
0.5117	13.50	42.0
1.222	32.34	41.9

The temperature was $E = 3.11$ expressed in Hefner candles; and therefore equal to about 1970°. The figures are sufficiently near the theoretical value (44). The fact that with the use of larger quantities of substance the figures become somewhat smaller, may perhaps be explained by the assumption that the oxygen of the air present is not entirely sufficient to prevent dissociation, but it is also possible that this is due to experimental errors.

(*2*) *Mercury.*—In the following experiments in which a substance was used which is not gaseous at ordinary temperature, like carbonic acid, the phenomenon was observed that the mercury meniscus which was depressed immediately after the introduction of the substance, moved afterwards slowly back, as will be seen from the following table:

Time in seconds.	Position of the mercury meniscus.
0	16.20
15	16.60
30	17.10
45	17.60
60	17.88
—	—
67	23.10
75	22.70
90	22.00
105	21.36
120	21.46

At 60 the substance was dropped in; it will be seen that the meniscus goes back first quickly and later slowly. The greater the quantity of substance used, the more the meniscus moves back.

The reason of this is scarcely to be found simply in the diffusion of the vaporized substance to the colder parts of the apparatus; it rather seems that the evaporation occurs so quickly, like an explosion, that a small portion of the substance is carried into the colder capillary part of the iridium vessel, the necessary result being that the readings become too small and hence the value of the molecular weights too large. As there was no better method available, the reading was extrapolated to the moment of the introduction of the substance, so that in the above case not 23.10, but 23.50 is chosen as maximum reading.

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With further improvements of the method, this error will be diminished or wholly removed; the figures of molecular weights, given in the following, may all be too high by some per cents., because the correction applied is evidently somewhat too small, and the error will be the greater, the greater the applied quantity of substance.

g.	*n.*	M.
1.069	5.62	213
2.308	11.40	226

The barometer reading was 738 mm., the temperature 14.0; the calculation was made by the formula

$$M = 1120 \frac{g}{n}.$$

E = 3.11, corresponding to 1970°.

(3) *Water.*—For the dissociation of this substance the same remarks are valid which were made on carbonic acid; the quantity of substance was introduced in form of a weighed piece of opal, the water content of which was found by the quartz balance to be 7.82, 8.22, 8.20, 7.63, 7.67; mean, 7.91.

g.	*n.*	M.
0.1596	9.8	18.4
0.1961	13.0	17.1

E = 11.2 (2142°), further H = 728, t = 15, hence

$$M = 1130 \frac{g}{n}.$$

(4) *Sodium Chloride.*—The substance vaporized rapidly also in this case, with a slight explosion; the values were

g.	*n.*	M.
0.1622	3.4	52.9
0.479	8.8	60.4
0.8645	15.2	63.1

The barometer and temperature were as in the carbonic acid tests. E = 3.11 (1970°).

(5) *Potassium Chloride.*

g.	*n.*	M.
0.700	9.54	81.5
0.818	10.6	85.6

E = 3.47 (1980°). Otherwise, what was said concerning sodium chloride, is valid here; in both cases if we except the first experi-

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ment with sodium chloride which is uncertain on account of too small a quantity of substance—the values are higher by 8 to 10 per cent. than the theoretical values (58.5 and 74.6 respectively). The normal molecular weight appears to be absolutely certain for these substances, especially if we compare these results with those with mercury in which the value was found to be too high by the same amount.

After the above experiments had been finished, I investigated, whether, as was assumed for the explanation of the results with mercury, there really takes place a transfer of a part of the vaporized substance to the colder parts of the apparatus, so that with a smaller speed of vaporization smaller values of the molecular weight would be obtained. For this purpose the iridium tubes were provided with strong plugs of zirconium pencils so that thereby the speed of vaporization was certainly diminished. The figures obtained, with $B = 752$, $t = 14.5$, $E = 2.72$ (1943°) were

g.	n.	M.
1.615	8.96	200
1.760	9.54	204

The approximation to the theoretical value (200) is now all that can be desired.

In this paper, I believe, I have given a relatively simple and certain method for determining molecular weights up to about 2200°; the further problem will be to refine the method and apply it to as many cases as possible. At the same time it may become possible to measure dissociation tensions, boiling-points and chemical equilibria up to such high temperatures. In performing these investigations, I was assisted with great zeal and interest by my private assistant, Dr. Riesenfeld.

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DISCUSSION.

[PRES. RICHARDS: The instrument Dr. Nernst has handed you is very brittle, so please take great care not to drop it (instrument passed about among the audience).]

DR. WILLIAM S. WEEDON: Mr. President, I wish to ask if Dr. Nernst has ever taken the vapor density of the double chloride of aluminum and potassium, or sodium.

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DR. NERNST: I have not made such measurements, I have only tried potassium and sodium chlorides.

DR. WEEDON: Prof. Remsen, of Johns Hopkins, was very much interested in the double salts and intended to make some experiments, but I do not think the work was ever completed. I was interested to hear, if you had made them, how the determinations had come out.

PRES. RICHARDS: There is quite a gap in our knowledge of the heats of formation of chemical compounds at high temperatures, and this may be partly made up by determining the dissociation of the products of combustion at these high temperatures. The products of combustion are mainly H_2O and CO_2 and CO, and by the use of such an apparatus the degree of dissociation of these gases at high temperatures can be accurately determined. We can then get an idea of the amount of heat which is generated in the reactions which form those gases, or which would tend to form those gases, at those temperatures; I foresee in the use of this apparatus, on those gases, the means of largely completing our knowledge of the thermal equation of electric furnaces.

PROF. W. D. BANCROFT: When we consider that at the ordinary temperatures we do not get very accurate vapor density determinations by the ordinary methods, it is indeed a pleasure and a surprise to see the way in which this method has been worked out, so that working with these infinitesimal amounts of substance, and at these very high temperatures, we get results which are apparently more accurate even than those we get under ordinary conditions. It seems to me that this investigation which Prof. Nernst has just described to us is indeed a triumph in every sense of the word.

DR. L. BAEKELAND: I wish to ask Dr. Nernst if he thinks that this apparatus can be used for determining the vapor densities of metals having high boiling-points; that is, would the metallic vapors destroy the apparatus or not?

DR. NERNST: (Replies in German.)

MR. A. H. COWLES: Dr. Richards, could we ask some one to translate those last remarks of Dr. Nernst?

PRES. RICHARDS: Prof Nernst states that it may be possible to use cadmium, from the fact that cadmium vapor may not alloy

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with the iridium at that high temperature, but that it would be necessary to use an indifferent atmosphere to exclude altogether oxygen, and to use possibly nitrogen or hydrogen as the gases with which to fill the apparatus. So far Dr. Nernst has confined his investigations to substances which do not unite with oxygen. He thinks that it may be quite possible to determine in the apparatus, in this manner, the vapor density for cadmium, zinc, sodium and potassium, and thanks the gentleman for the suggestion.

If there are no further remarks, I will express to our distinguished guest the thanks of the Society for his very interesting communication. (Applause.)

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

CONSTANT VOLTAGE AND CONSTANT CURRENT SEPARATIONS.

By Wilder D. Bancroft.

Since the electrolytic separation of two metals depends on the fact that one precipitates at a lower voltage than the other, it would seem as though the proper way to effect a separation were to hold the voltage at a value such that the second metal cannot precipitate. This method of constant voltage separation was first introduced as a general method by Freudenberg.[1] It has the advantage that the current drops to a very low value as soon as the first metal is completely precipitated, thus giving an automatic indication of the degree of precipitation. Since the second metal cannot precipitate under the conditions of the experiment, the current may be allowed to run all night if necessary. As a matter of fact, this method is not used in most of the standard separations, which are rather to be classed as constant current separations, even though the current may not be held absolutely constant. In order to prevent the second metal precipitating as soon as the first is all down, it is necessary that hydrogen shall be set free by the current instead of the second metal. The essential feature, therefore, of a constant current separation is that the decomposition voltage for hydrogen in any solution shall lie below the decomposition voltage of one of the two metals. Since most separations were originally made without a voltmeter in circuit, no satisfactory results were obtained until a solution was found which permitted of a constant current separation and, for this reason, all except some of the most recent separations are constant current separations. The importance of hydrogen and the resulting distinction between a constant voltage and a constant current separation was recognized by Freudenberg[2] and less clearly by Neumann,[3] but has been generally overlooked. In fact, there are no data showing

[1] Ztschr. phys. Chem., **12**, 97 (1893).
[2] *Ibid.*, **12**, 103 (1893).
[3] "Electrolytic Analysis," p. 166.

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the facts for solutions of cyanides, oxalates, phosphates, and tartrates.

In Tables I-V are shown the order of the metals in solutions of sulphates, nitrates or chlorides, cyanides, oxalates, phosphates, and tartrates. The data in Table I are based on Neumann's electromotive force measurements with the exception of the first hydrogen value which refers to the electrolysis of a magnesium sulphate or sodium sulphate solution. Tables II-V are based on experiments by Mr. Root which will be published later. A cross against a metal means that metal does not precipitate from that solution at any current density ordinarily employed in electrolytic separations. The metals were added in the form of sulphates, chlorides, or nitrates, as was most convenient. The hydrogen values in Tables II-V are the decomposition values of the solution without addition of metallic salt. Where two or more metals are bracketed, the decomposition voltages are very close together.

TABLE I.

Sulphates, nitrates, or chlorides.
1 M. wt. metal/liter.
20°.

Hydrogen.
Zinc.
Cadmium.
Iron.
Nickel.
Lead.
Hydrogen.
Tin.
Bismuth.
Copper.
{ Mercury.
{ Silver.

TABLE II.

n/4 KCN.
0.2 gram metal/200 cc.

20°.	60°.
Iron x.	Iron x.
Nickel x.	Nickel x.
Zinc x.	Zinc x.
Copper x.	Cadmium.
Cadmium.	Copper.
Hydrogen.	Hydrogen.
Bismuth.	Bismuth.
Mercury.	Mercury.
Silver.	Silver.

TABLE III.

150 cc. ammonium oxalate, saturated at ordinary temperature.
0.1 g. metal/175 cc.
60°.

Zinc.
{ Iron.
{ Nickel.
Cadmium.
Lead.
Hydrogen.
Bismuth.
Copper.
Mercury.

TABLE IV.

50 cc. Na_2HPO_4(1.025).
15 cc. H_3PO_4(1.3).
0.1 g. metal/150 cc.
60°.

Iron x.
Nickel x.
Tin x.
Zinc.
Cadmium.
Lead.
{ Hydrogen.
{ Bismuth.
Copper.
Mercury.
Silver.

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TABLE V.

7.5 g. cryst. tartaric acid.
35 cc. ammonia (0.92).
0.1 g. metal/170 cc.
60°.

Tin x.
Zinc.
Nickel.
Hydrogen.
Bismuth.
Copper.

In Table I the position of hydrogen can be changed from below lead to above zinc by passing from normal sulphuric acid to normal magnesium sulphate or sodium sulphate. From Table II we see that iron, nickel, zinc, and copper do not precipitate at these concentrations from N/4 KCN at 20°, but that copper precipitates at 60°. By using a more dilute cyanide, zinc will precipitate while iron does not. The bismuth solution had citric acid and alkali added to it. The presence of cadmium, curiously enough, seems to raise the decomposition voltages of the cyanide and oxalate solutions so that cadmium precipitates before hydrogen in both these solutions though at a higher voltage. Tin and zinc will precipitate from a more dilute alkaline tartrate solution.

TABLE VI.

Silver or mercury from :				Copper from :			
Cu.	Nitric acid.	V.	P.	Bi.	Cyanide + citrate, bismuth ppts.	C.	H.
	Cyanide.	C.	H.	Pb.	Excess nitric acid.	C.	H.
Bi.	Nitric acid.	V.	P.	Sn.	Tartrate + NH_3.	C.	H.
Pb.	Excess nitric acid.	C.	H.	Fe.	Acid.	C.	H.
Sn.	Ag_2S insoluble.				Phosphate.	C.	H.
	Sulphide.				Oxalate.	C.	H.
Fe.	Nitric acid.	C.	H.	Ni.	Acid.	C.	H.
	Cyanide.	C.	H.		Phosphate.	C.	H.
Ni.	Acid.	C.	H.		Oxalate.	V.?	H.
	Cyanide.	C.	H.	Cd.	Acid.	V.?	H.
Cd.	Nitric acid.	C.	H.		Phosphate.	C.	H.
	Cyanide.	V.?	H.		Cyanide, cadmium ppts.	C.	H.
Zn.	Cyanide.	C.	H.	Zn.	Acid.	C.	H.
					Phosphate.	C.	H.

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TABLE VII.

Bismuth from :				Iron from:			
Pb.	None.			Ni.	None.		
Sn.	Tartrate + NH_3.	C.	H.	Cd.	Alkaline cyanide, cadmium ppts.	C.	H.
Fe.	Acid sulphate.	C.	H.		Ammonium sulphate + sulphuric acid, cadmium ppts.	C.	?
Ni.	Acid sulphate.	C.	H.		Phosphate, cadmium ppts.	C.	H.
Cd.	Acid.	C.	H.	Zn.	Alkaline cyanide, zinc ppts.	C.	H.
Sn.	Acid.	C.	H.				

TABLE VIII.

Nickel from :				Cadmium from :			
Cd.	Alkaline cyanide. cadmium ppts.	C.	H.	Zn.	Sulphate.	C.	H.
	Ammonium sulphate, + sulphuric acid, cadmium ppts.	C.	?		Cyanide.	C.	H.
					Oxalate.	C.	H.?
Zn.	NaOH + tartrate, zinc ppts.	C.	H.		Phosphate.	C.	H.

In Tables VI-VIII are given the majority of the separations for silver, mercury, copper, bismuth, tin, lead, nickel, iron, cadmium, and zinc. The second column gives the solution. In the third column, V denotes a constant voltage separation and C a constant current separation. In the fourth column, H denotes that hydrogen is evolved instead of the second metal, while P (potential) denotes that this is not the case. Unless some disturbing factor enters in, the P's and V's should go together and the C's and H's. The first thing to be noticed is that the overwhelming majority of these separations can be run at constant current without reference to the voltage.

I have no data for the separation of mercury from tin in the sulphide solution, but it is probable that it is a constant current separation under these conditions. According to Mr. Root's measurements, the decomposition voltage for iron and nickel in an acidified ammonium sulphate is but little higher than that of cadmium when the solution contains 10 grams ammonium sulphate and 4 cc. sulphuric acid (1.09). It seems doubtful whether a separation can be effected without the use of more acid. The separation of cadmium from zinc in oxalate solutions appears to be due to the fact, previously stated, that cadmium seems to raise

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the decomposition voltage for hydrogen. The separation of cadmium from zinc is actually made in a phosphate solution containing less phosphoric acid, but the general relations remain the same. Nickel and zinc cannot be separated in an ammoniacal tartrate solution, but the separation is satisfactory when caustic soda is used, since no nickel precipitates at the cathode.

These apparent exceptions and the precipitation of zinc from alkaline cyanides and alkaline tartrate solutions become intelligible when we take into account the solutions actually used. There remain three fundamental exceptions, the separations of copper from nickel in oxalate solutions, of copper from cadmium in acid solutions, and of silver from cadmium in cyanide solution. All three should be constant current methods and all three require regulation of the voltage. It is probable that the explanation is the same in all three cases, the formation of a compound or solid solution of the two metals so that the less noble metal precipitates as a compound or solid solution at a voltage at which it could not come down as pure metal. I have myself observed an electrolytic precipitation of brass at voltages at which zinc alone will not precipitate and we are all familiar with the lowering of the decomposition voltage when the precipitating metal can alloy with the cathode.

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DISCUSSION.

DR. N. S. KEITH: Mr. President, I would ask Prof. Bancroft whether his experiments were carried on with insoluble anodes in the electrolysis of various solutions?

PROF. W. D. BANCROFT: These were all done under the conditions under which they would be done in electrolytic analysis; that is, with platinum dish as cathode, platinum anode, and the electrodes a definite distance apart, so we had all our conditions carefully specified. These will be given in Mr. Root's paper.

DR. LEO BAEKELAND: I would ask Prof. Bancroft whether he has any data on cyanide solutions of uranium salts in conjunction with silver. I have used voltages as high as four volts with uranium compounds and I wanted to ask Dr. Bancroft whether he had any data in regard to uranium compounds. When my voltage went

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to about 2, I was able then to avoid the precipitation of uranium.

DR. BANCROFT: I have made no experiments with uranium salts. My object in doing this work was merely to go over the ground covered in ordinary analyses and get the subject on a systematic basis so that my students would understand what were the general principles underlying the separations. At present the text-books on electrochemical analysis consist of a collection of directions; the subject is not classified, and there are no data to enable one to classify it.

MR. CARL HERING: As Dr. Bancroft used insoluble anodes the solutions will necessarily change quite decidedly during the test, and therefore, after a test has progressed, he will no longer have the same composition of solutions as he had at the start. The figures that he gave concerning the composition can therefore apply only to those at the start.

MR. REED: I would ask Dr. Bancroft whether he considers the deposition of lead peroxide from lead nitrate at the anode, an electrochemical action, in distinction from a purely chemical or thermochemical action. Perhaps I can explain what I mean by an illustration: If a piece of zinc is inserted at the top of a solution of sulphate of copper it will chemically remove the copper in its immediate neighborhood. Then the action will stop until diffusion alone brings more copper to the plates. Now I would ask Dr. Bancroft if he considers that that is the kind of a reaction which takes place in the electrolytic deposition of lead peroxide in nitric acid solution, whether it is really an electrolytic action and will proceed by the migration of material in the ordinary electrochemical sense to the anode, or whether it will stop after a certain time.

DR. BANCROFT: Mr. Hering is of course entirely right in saying that the composition of the electrolyte will change and that the voltage will change. The composition of the solution must change if in the course of the analysis we are going to get out the whole of the metal, and that is one reason why I have not given any quantitative values. I have simply called attention to the order in which the metals precipitate, and that is unchanged throughout the course of the analysis, so that this order is all right in regard to the actual analyses. When it comes to the question as to how lead peroxide precipitates at the anode, that is a point which is a little outside of

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the question of the theory of electrochemical analysis; but, personally, I look upon it that it is an electrochemical precipitation, just exactly as the precipitation of lead or other metals at the cathode; and I should not class it as in any way a chemical—purely chemical action. On the other hand, of course, as we all know, it depends very largely on how we define things, whether we are going to call them electrochemical, electrothermal or chemical; so I can merely state my opinion of it in regard to the definition that I give to the word, which may or may not be the same as the definition of Mr. Reed.

DR. H. S. CARHART: The separation of pure cadmium from an alloy containing small quantities of zinc is very important in order to obtain pure cadmium for the making of Weston cells. Prof. Bancroft made just a passing reference to the separation of cadmium from zinc by a constant current. In the separation to which I refer we had a soluble anode consisting of cadmium with a trace of zinc. I find what is called pure cadmium obtained from German chemical manufacturers contains, at least in some cases, an appreciable quantity of zinc. I should like to inquire, therefore, if Prof. Bancroft can give any specific directions for the separation of pure cadmium from this alloy.

DR. BANCROFT: I cannot. I was interested here in taking things as they occurred in the books on electrochemical analysis. One gets the cadmium down with a sufficient degree of accuracy for the purposes of analysis and whether one can do more than that I don't know. I should be inclined to think at any rate, however, that if even the zinc does come down with the cadmium, a series of fractional precipitations in cyanide solutions would certainly free the cadmium from zinc. Zinc itself does not come down in the N/4 potassium cyanide solutions. That would not prove that it might not come down with the cadmium if it formed a solid solution with it, which, of course, is quite possible, in view of the similarity of the two metals. I should be inclined to suppose that there would be relatively little zinc in the cadmium and that a second electrolysis would separate it.

This brings up the whole question of precipitation of compounds and solid solutions about which, I am sorry to say, we do not yet know as much as we shall. We know that we can precipitate brass

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from a cyanide solution at voltages below which the zinc alone will precipitate. Why we cannot get brass, to a certain extent, from an acid solution I do not know. Several people have stated that they have obtained brass from an acid solution of zinc and copper; but I think that in all those cases the identification was based on color, and color is not a very satisfactory test for brass, as I know to my sorrow.

MR. GEO. M. HOWARD: Has Prof. Bancroft done anything on alkaline sulphides, on antimony, tin and arsenic?

DR. BANCROFT: No, I have done nothing with those solutions.

MR. REED: I would call attention to a statement recently made in *Electrochemical Industry* by Mr. W. McA. Johnson, that copper in a cyanide solution precipitates zinc. It seems to me that that was a rather remarkable statement, but on trying the experiment I found, by taking a very strong solution of potassium cyanide on one side of a porous wall and a strong solution of zinc sulphate on the other side and bending a piece of copper around so that it dipped into both solutions, forming a local circuit, that copper dissolved in the cyanide and zinc deposited from the zinc sulphate solution, showing that in that particular combination copper will precipitate zinc, whereas, in almost all cases zinc precipitates copper.

MR. F. M. BECKET: In regard to the deposition of copper and zinc, I might say that I have frequently deposited these metals simultaneously as brass from sulphuric acid solutions in sufficient quantity for accurate chemical analysis. The result, therefore, was not judged by color. By varying the current density the percentage composition of the alloy was changed considerably, as was also proved by chemical analysis. This deposition cannot be kept up very long, not more than two or three hours, particularly if the solution is not agitated. This is not a practicable method, but the results may be obtained for a short time.

DR. BANCROFT: I have tried that same experiment, perhaps not under as favorable conditions, and I obtained a simultaneous deposit of copper and of zinc, and in one place there was something that looked like brass; but upon examining it under the microscope I came to the conclusion that we had simply a mixture of copper and

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zinc, which, of course, would analyze exactly the same way as brass, and that we did not have brass there. I am rather confirmed in my view by the fact that one cannot go on plating the electrode to an indefinite thickness. It may be that there were certain conditions which we failed to observe, in which case I should be very glad to learn of that later. There is no difficulty in precipitating both zinc and copper from a sulphate solution. There is also no difficulty in getting a substance which looks like brass, but whether it actually is brass is a point on which I have been very doubtful.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

AN EXPERIMENTAL STUDY OF SOME ELECTRODE EFFECTS.

By H. M. Tory and H. T. Barnes.

During the course of a preliminary investigation into the change in the molecular complexity of water above and below the point of minimum specific heat, which we have been recently carrying on, we found it necessary to work with plain platinum electrodes in pure water. The difficulty of bringing such electrodes to zero potential is well-known, and we were no more fortunate than others in this respect. We observed variations which we found were connected in some way with either a change in the temperature of the electrodes, or a change in the state of the water, or with the heating of the electrodes before inserting in the water.

From a knowledge of the occlusion of air by platinum, it might at first sight appear obvious what would happen as a result of any one of these changes, but when such electrodes are actually used it is not by any means so simple a problem.

Such expedients as tying the electrodes together over night, or platinizing, or both, or saturating with gases, are found to be only temporarily effective. When other metals are used as electrodes no better or steadier results are obtained, but small potentials varying either one way or the other are found to exist.

It became necessary for us therefore to make a study of these irregularities in order to measure the effect we were looking for. We undertook a special series of experiments, which series forms the subject, in brief, of the present paper.

We soon found, not only with platinum, but with all other metals that we tried, that the small variations in the electrodes were connected not only with the occlusion of gases, but also with the presence of these gases dissolved in the water.

We found large potential differences between two electrodes of the same metal, one in boiling water and the other in water through which air, oxygen or hydrogen had been passed.

No difference of potential was observed, however, between

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boiling water and cold water if the latter had also been boiled and freed from dissolved gases before being used. Although at first small differences of potential were observed between one platinum electrode which had been heated, and one which had not been so heated, both in air-free water, these differences disappeared on standing in the water for a little time. One of our first experiments was made with two platinum electrodes, one in flowing air-charged water and the other in quiet water, surrounded by a temperature jacket. It was found that the potential gradually increased as the temperature of the quiet water was raised, giving us a perfectly regular curve convex to the axis of temperature. On cooling the jacket again we found that the electromotive force between the electrodes did not return to zero until fresh air-charged water was introduced around the electrode. It was evident from this experiment that the quantity of air in the water determined the electromotive force. The potential of the electrode in the air-charged water was positive to the electrode in the air-free water. The rise of the electromotive force with temperature meant the discharging of air from the water, and the fact that the electromotive force would not return to zero on cooling showed us that the cool water was still air-free. We found that this experiment could be repeated more easily with aluminum electrodes, since the tenacity with which platinum occludes air sometimes gives rise to irregular results.

As soon as we were convinced that air was the cause of the large potential differences we had observed, on our various electrodes, we undertook to measure the potential differences for a large number of metals, in pure water charged with either air, oxygen, or hydrogen against air-free water. We obtained the potentials on an Edelmann quadrant electrometer, which gave us about 74 millimeters for 1 volt. The apparatus consisted of a vertical glass tube, provided with a lower and an upper inflow tube, with an outflow tube in the middle.

Pure distilled water, after having been boiled vigorously in a 5 liter Jena flask for several hours, was passed through a cooler and introduced into the apparatus at the lower inflow tube at a temperature below the temperature of the room.

The outflow could be regulated so as to maintain a column of air-free water in the upper part of the apparatus. When desired,

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this could be replaced by air-charged water at a slightly higher temperature, through the upper tube. The difference in temperature kept the air-free and air-charged water sharply separate at the outflow. This could be seen by the difference in refractive index. When oxygen or hydrogen was used the gas was bubbled through the water in the upper part, while the lower water was kept running slowly. One electrode was placed in the upper half of the apparatus, and the second electrode was placed in the lower portion.

Thermometers were placed in side tubes, to record the temperature of the upper and lower halves. Two other side tubes bent at an angle of 30°, and rising as high as the top of the apparatus, served as openings through which the electrodes could be introduced or interchanged at will.

We used various other forms of apparatus, but this proved to be the most serviceable.

The following table contains the results we obtained for a number of metals. Each result is for two electrodes of the same metal.

TABLE I.—E. M. F. IN VOLTS.

Metal.	Air-charged against air-free.	O-Charged against air-free.	H-Charged against air-free.
Aluminum	0.74 to 0.80	0.810	0
Cadmium	....	0.125	—0.036
Carbon filament	....	0.092	—0.175
Copper	0.141	....	0
Gold	0.170	....	0
Iron	0.284 to 0.240	0.240	0
Lead	0.074	....	0
Palladium	0.205	0.205 to 0.235	—0.640
Platinum	0.226 to 0.212	0.210	—0.445 to 0.308
Silver	0.105	0.081	+0.082
Tin	0.27	0.27	0
Zinc	0.38	0.38	+0.181
Magnesium	0.020	....	—0.206
Mercury	0.068	....	0
Nickel	0.151	....	—0.151

As a rule we found the O-charged to be the same as the air-charged. In every case, except where a negative sign is attached, the electrode in the gas-charged is positive to the electrode in the gas-free. The reverse is the case through the water. In hydrogen we find some metals positive and some negative, but mostly neutral. In every case except where the metal is attacked by air-

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free water the electromotive force is immediately brought to zero by surrounding the electrodes with air-free water. The same result is achieved by heating the water around the electrode to boiling, so as to expel the gas.

From these results it appeared to us that we had to do with a process of occlusion, rather than with a process of oxidation or reduction. Summarizing, we found that the potential was brought to zero in air-free water; that the most easily oxidized metal in our series, magnesium, gave the smallest value with oxygen; that an aluminum electrode artificially oxidized gave against a clean aluminum electrode in air-free water, an electromotive force one-half the observed value given in the table; and that the metals which occlude the largest quantity of gas such as platinum and palladium are the most difficult to bring to zero potential.

We next made some experiments to test these results for dissimilar electrodes. The potential between two different metals in air-free water was measured on the electrometer, and oxygen or hydrogen gas was then bubbled through the water around both electrodes. The resulting change in the electromotive force was measured. We found that this change could be calculated from Table I. We give some results obtained from an electrode of silver and one of zinc. In air-free water, silver was positive to zinc, 1.02 volts. In oxygen-charged water this was reduced to 0.73 volt, and in hydrogen-charged water it became 0.87 volt. This relation may be seen as follows:

$$\begin{array}{ccc} Ag(O) & + 0.105 & Ag \\ + & & + \\ 0.75 & & 1.02 \\ Zn(O) & + 0.38 & Zn \end{array}$$

Ag(O) stands for silver in oxygen-charged water while Ag stands for silver in air-free water. The value + 0.105 is taken from Table I. Zn(O) is + 0.38 to Zn in air-free water. This gives for Ag(O) against Zn(O) the value + 0.75 instead of the observed value + 0.73 volt.

For hydrogen a similar scheme gives + 0.92 calculated from Table I instead of + 0.87 observed.

Although the agreement is not perfect yet it shows no wide difference from the additive relation expressed above.

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For aluminum and magnesium we find the following cycle:

$$\begin{array}{ccc} Al(O) & + 0.80 & Al \\ + & & + \\ 0.986 & & 0.206 \\ Mg(O) & + 0.02 & Mg \end{array}$$

This gives in oxygen-charged water the value + 0.986 while the value actually observed was 0.989.

We have tried a number of other combinations such as lead and aluminum and find that the electromotive force between them in air-free water is reduced almost to zero, when oxygen is bubbled through. In every case it is possible to predict what the change will be and in what direction. Some electrodes reverse in polarity while, as we see, some separate and some come together.

Warburg[1] and Markovosky[2] have observed a similar effect for electrodes in salt solutions, and for dilute sulphuric acid. The explanation given by these observers for the electromotive force developed on Pt, Hg, Cu, Zn and Ag electrodes in air-free sulphuric acid and air-charged acid is that the metal dissolves on the side containing the O more readily than on the side containing no O. This sets up a concentration cell with the sulphate of the metal in solution. For hydrogen the reverse takes place at the gas electrode, and a reduction of the salt already present takes place with the formation of sulphuric acid. The proof offered by Markovosky is briefly as follows, based on his experiments for Pt electrodes; platinum sulphate added to the air-free side of the concentration cell brings the electromotive force down; heating the oxygen-charged side to 70° C. does not alter the electromotive force, and changing the pressure of gas over the solution from 20 mm. to 2½ atmospheres does not alter the electromotive force.

We do not wish at this time to express an opinion in regard to the strength of these arguments because as yet, we have not used dilute sulphuric acid in our experiments, but we may state as far as our experiments go that both for platinum and aluminum electrodes in water the electromotive force varies with the temperature at which we saturate the water. For two platinum or aluminum electrodes, and the same would be true for other electrodes, the electromotive force between air-free water and oxygen-

[1] Pogg. Ann., 38, 321 (1889), and 41, 1 (1890).
[2] *Ibid.*, 44, 457 (1891).

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charged water may be reduced slowly by driving out the oxygen by heat, and subsequently reduced to zero by boiling without changing the water.

In conclusion, we may state that further experiments which we have been unable to communicate in this paper on account of the stress of other work, and which we hope to communicate in a later paper tend to support the view that for pure water at least, we are probably dealing with an occlusion phenomenon.

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A paper read by title at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1902, President Richards in the Chair.

FREE IONS IN AQUEOUS SOLUTIONS.

By W. R. Whitney.

The purpose of this paper is to briefly discuss the results of some experiments on this subject which were described by Olsen in the *American Journal of Science,* **14**, 237 (1902). The author has attempted to so modify the historic experiment of Ostwald and Nernst[1] as to show by the influence of a statically charged mass near a solution that the ions within the solution may be made to separate positive from negative, and to collect in those parts of the solution determined by the location and sign of the charged electrophorous plate. Ostwald and Nernst observed the formation of gas on the mercury surface of their electrometer; this made it appear that an electrolysis had been brought about by induction produced by the introduction into the vicinity of the solution of an electrostatically charged surface. Olsen inclines to the belief that in this case the effect was due to simple conductivity or leakage of the static charge from the charged surface.

In Olsen's first experiment a vessel containing dilute sulphuric acid and two sheet platinum electrodes was so placed with respect to an external, electrostatically charged surface at the side of the beaker or vessel that the electrodes were both at right angles to this surface. After allowing the static charge to act for a time it was removed and the electrodes as a whole rotated within the solution through 90° so that one of them was brought near to the previous position of the charged surface, and the other one further away from it. That is, the electrodes were gently moved into those parts of the solution into which the ions if electrostatically charged and capable of moving should have passed, under the influence of the statically charged surface. In this case, a current was set up through the galvanometer in the circuit connecting these two platinum electrodes, which is in accord with the theory of charged ions. It is not clear how the effect of leakage of the

[1] Zeitschrift für physikalische Chemie, 3, 271 (1889).

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static charge from the surface of the electrophorous is made less objectionable than it was in the experiment of Ostwald and Nernst where the observed effects the author considers ascribable to leakage rather than to induction. The author was obliged to continually recharge his charged surface to make up for its leakage and if this leakage could account for the phenomena observed then the weight of this experiment as a proof of the existence of electrostatically charged ions is reduced. While it is perfectly true that electrochemical phenomena are most readily explained by the assumption of charged ions, and, while many investigators are firm in their belief in the actual existence of such charged particles, an experiment actually proving their existence would be of great interest. This first experiment of Olsen does not seem to me to be free from objection and it seems possible that ordinary electrolytic conductivity could account for the results he obtained. Leakage of electricity of high electromotive force taking place through the space surrounding the charged surface would doubtless distribute itself through the neighboring conductors in accord with Ohm's Law, and the electrodes in the solution used in the experiment would then become in part conductors of this feeble current. As they were placed in respect to the charged surface, both electrodes should conduct equally and the potential drop take place along them in the general direction away from the charge. As this involves difference of potential along the surfaces of these electrodes it is certain that they would act as will an isolated piece of wire suspended in the midst of an electrolyte which is carrying a current; that is, the opposite ends would act as electrodes of opposite sign and electrolysis take place. It is not to be expected that such electrolysis as is due to leakage of this static charge would produce visible gas bubbles, for though the potential drop is great, the quantity factor is very small. It must be great enough however to produce some electrolysis and thus the solution adjacent to the two ends of the pair of electrodes would be charged with the products of the polarization, *i. e.*, hydrogen and oxygen. When now the electrodes (which have been so affected by the leakage as to be alike,—positively polarized at one end and negatively at the other) are moved through 90° and connected through a galvanometer, it seems probable that one of them is practically bathed in a part of the solution which contains some free hydrogen

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from the electrolysis referred to, and the other is similarly an oxygen electrode of low concentration. If this is true to any extent whatever, the results actually obtained would be explained without the necessity of electrostatically charged ions, for it is known that like electrodes in unlike solutions always show differences of potential. The observations made would have certainly been the same if an appreciable electric current had been passed for an instant through the solution parallel to the electrodes, and these electrodes had then been turned through 90° and the measurements made as described. It is therefore only necessary to admit the passage of a current due to leakage of the charged surface to make the proof of statically charged ions in the solution questionable.

Another experiment described by Olsen consisted in subjecting a diluted aqueous solution to the action of a current of less than one volt intensity, and after cutting out this current the potential difference between the portions of the electrolyte near to the electrodes was observed by means of a galvanometer connected to secondary or exploring electrodes which were placed near the primary electrodes. The conclusion is drawn that—"This would show that the liquid in the neighborhood of a positive pole connected to a Daniell is charged with positive ions, or around the negative pole is charged with negative ions, or both."

It seems to me that the presence of dissolved products of electrolytic decomposition explains the observations without reference to ions.

It is known that low voltages cause electrolysis of aqueous solutions even when much below the voltage necessary for visible decomposition and it is not strange that the hydrogen and oxygen polarizing the electrodes dissolve in the electrolyte. The measured potential difference observed would be expected, as it would be found in any case of platinum electrodes dipping into separate solutions containing free hydrogen and oxygen. Gaseous products deposited on electrodes differ from metals so deposited, in that such gases even at low pressures corresponding to low values of impressed electromotive forces may appreciably dissolve in the electrolyte in which metals are practically insoluble.

The effect of electrostatic charges adjacent to a solution subjected to low electromotive forces was also studied by Olsen and

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similar results found. The author's conception is "that either the ions are heaped up about the electrodes as they become charged by the current or the current although below the decomposition value for the evolution of gases yet decomposes the electrolyte," the idea being that this decomposition is simply an additional dissociation instead of a simple electrolysis. Therefore the experiment was repeated with fourteen-hundredths normal sulphuric acid solution where the dissociation is already practically complete. The results being the same as before, the author says "Here no decomposition of the sulphuric acid could take place as it was completely dissociated before, and the voltage was too low to decompose the water,—hence it would seem that there are free ions present and that they are heaped up around the electrodes when they are charged by a Daniell." Here again the fact that a current is known to pass through solutions under such circumstances makes the production of molecular hydrogen and oxygen seem an absolutely necessary consequence; and this admitted, the observed phenomena of potential differences between electrodes placed in separate parts of the solution together with the nature of the sign, is what would be expected, without reference to statically charged ions.

Copper electrodes in copper sulphate solution were also subjected to the influence of electrostatically charged surfaces outside the solution, the charged body being so connected to the Leyden jars of a static machine that the charge which leaked away could be resupplied. In this case one electrode gained and the other lost in weight by about a milligram. It seems that these experiments show that there is simply an electrolytic conduction through the electrolyte in each case. The leakage of the static charge from the charged surface might be expected to take place through the solution to an extent such as observed. Leakage occurs and must be expected to involve electrolytic conductivity through an electrolyte between electrodes when these are not both at points of identical potential in the field through which the leakage occurs.

The conclusions drawn that the solutions behave "as if they contained particles charged with electricity, which are free to move and which may be moved by an electrostatic charge," may not be erroneous, but that the solutions contain electrostatically charged particles is not a necessary conclusion from the experiments.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, Vice-President Bancroft in the Chair.

THE ELECTROLYSIS OF WATER.

By Joseph W. Richards and Walter S. Landis.

The phenomena accompanying the passage of an electric current through acidulated water have been studied from the very beginning of electrochemistry. It is believed that a true explanation of them would clear up a great deal of the present incomplete state of our knowledge of the subject of electrolysis in general. Omitting the experiments of the early investigators, which were intended solely to show the actual decomposition of water, we will here review the work of a few of the later ones.

Helmholtz[1] was probably the first investigator to observe the passage of a current through water at a voltage below 1.5 volts. He mentions that a Daniell cell passed current through water for four or five months without visible decomposition. His results were somewhat incomplete because of his lack of measuring instruments.

Ernst Salomon[2] first developed, at the suggestion of Nernst, the idea that when using soluble electrodes, the difference of concentration produced at the two electrodes gave rise to an electromotive force whose intensity could be calculated from the difference in concentration at the two electrodes and the rate of diffusion of the salt in the electrolyte.

Sokolow[3] claims to have produced hydrogen gas bubbles on a platinum cathode by using 1.072 volts.

H. Danneel[4] took up Nernst's idea, as used by Salomon, and applied it to calculating the residual currents which pass through dilute aqueous solutions of acids and bases, from which higher

[1] Pogg. Ann., 150, 483 (1873); Wiss. Abhandl., I, 823.
[2] Zeit. für Elektrochemie, III, 264 (1896).
[3] Wien. Ann., 58, 209.
[4] Zeit. für Elektrochemie, IV, 211, 227 (1897).

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voltages liberate hydrogen and oxygen. Danneel based his calculations on Fick's Law of the diffusion of a substance in a fluid,

$$S = \frac{q}{l} \cdot D(C_1 - C_2)Z,$$

in which S is the quantity of substance diffusing through a length l of solution, with a cross section q, in time Z (in days), with concentrations C_1 and C_2 at the respective terminals (in grams per cubic centimeter), and D is the quantity found by experiment diffusing through a 1 cm. cube, in one day, for a difference of concentration of 1 gram per cm. cube.

Since hydrogen diffuses so much faster than oxygen, the calculations were made for hydrogen, on the assumption of the solution being saturated at one pole (0.000002 gram per cubic centimeter) and containing no hydrogen at the other pole, and taking D as 4, from Hufner's figures. Calculating on the basis of oxygen diffusing from one electrode to the other, the saturation point is 0.000041 gram per cubic centimeter and D = 1.62.

Experiments were then made with dilute sulphuric acid, and the currents passing measured for voltages up to 0.08. The actual residual current measured was two to five times the calculated value for electrodes close together, and up to fifty times as much, for electrodes 26 cm. apart. It is to be regretted that the measurements were not made with higher voltages also. Danneel cannot be said to have proven his thesis.

Glaser[1] investigated at length the question of the passage of these residual currents. His first research was on the electromotive force of the gas battery. He made this to be over 1.09 volts, with a tendency to slowly reach a higher value. He then investigated the current passing through dilute sulphuric acid (N/10) with increasing voltages up to 1.20. His curves show a rapid increase in current, or nick in the curve, at 0.59 volt, and again at 1.09 volts, when the two electrodes used were of equal size. When the anode was large and the cathode small, a sudden rise occurred between 0.7 and 0.8 volt, and another at 1.10 volts. Other tests, however, showed only the rise at 1.10 volts, without any explanation of the absence of the lower bend in the curve. With dilute alkalies there was a slight rise at 0.5 to 0.6 volt and a decided rise at 1.10. By using a large cathode and small anode,

[1] Zeit. für Elektrochemie, 4, 355, 373, 424.

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the curve began to rise steeply at 0.7 to 0.8 volt, and became nearly linear above 1 volt. Using caustic potash, a marked nick or turning point in the curve was found as follows:

With	10	normal	KOH	at	1.32 volts
"	4	"	"	"	1.38 "
"	1	"	"	"	1.40 "
"	$1/_{8}$	"	"	"	1.45 "
"	$1/_{80}$	"	"	"	1.46 "

using a small cathode and a large anode.

Glaser's results were not conclusive since they neither show the cause of the residual currents nor their properties.

Emil Bose[1] has published a long and very interesting work on the decomposition voltages. He used a continuously increasing voltage, so that increasing measurements were obtained without breaking the circuit. He started out first to test Glaser's results, using electrodes of unequal size. He remarks that decomposition points are much more difficult to detect when gases are evolved, than when solids only are deposited. He found in five experiments a gradual bend in the current curve at the neighborhood of 1.08 volts, but not the sharp bend indicated by Glaser. Bose suggests the most probable value of this point of the reversible decomposition and formation of water, as 1.14 volts.

Bigelow[2] has made extensive tests, keeping the voltage constant at one volt, and measuring the current for as long as 82 days. The residual current falls for 50 to 70 days, from which it would appear that no one before him had measured the true residual currents. The values reach a minimum which Bigelow takes to be the true residual current. With platinum electrodes 17 mm. square and 11 mm. apart, in sulphuric acid (0.05 per cent.), the residual current, in micro-amperes, was 56.4 at the end of twenty-four minutes, but sank to 0.169 in seventy-two days. These results invalidate the figures of all previous investigators, since they measured their currents at thirty seconds or one minute in some cases, at five to twenty-four days in others.

We shall now take up in detail the experiments which we have made at the laboratory of the Lehigh University with a view of throwing some light upon many of the obscure points untouched upon by these previous investigators. It may seem strange to

[1] Zeit. für Elektrochemie, 8, 153.

[2] Journal of Physical Chemistry, Vol. 6, No. 9.

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many to notice the widely varying experiments which we made, but we may say, as others may have already experienced, that each experiment led up to several others; in fact to a sort of a divergent series of experiments, and it is only the most striking which we have here reproduced. Following the scheme of presentation of the work of the other investigators we shall first describe the experiments and then return to a critical and comparative review of them afterwards.

ELECTROLYSIS IN CLOSED VESSELS.

Dilute sulphuric acid (0.1 per cent.) was boiled to expel dissolved gases, cooled in a closed vessel, and electrolyzed in thermometer bulbs, completely filled and sealed as full as possible. In every case, when a current at 3 volts tension was applied, the bulb exploded within thirty seconds, and it was impossible in this time to follow the course of the ampere meter. The apparatus was arranged as the upper design in Fig. 1.

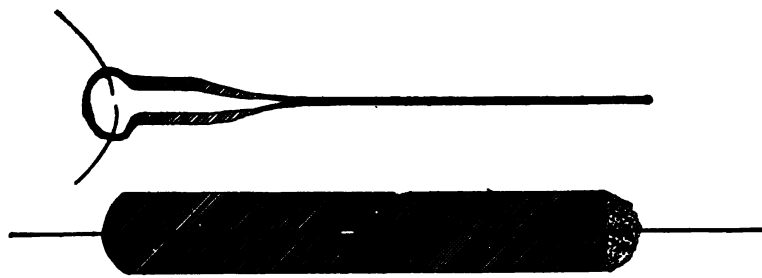

FIG. 1.

The platinum wires (⅛ mm. in diameter) were then sealed inside a thermometer stem with a bore ¼ mm. in diameter and with walls 2½ mm. thick around that bore. (See lower design, Fig. 1). Theoretically this should stand 25,000 atmospheres,—much more than the pressure of water if converted into hydrogen and oxygen in its own volume (1,830 atmospheres). The tube was filled, the platinum wires being within 1 mm. of touching each other and sealed by Canada balsam at the ends, without an indication of any clear space. Three and one-half volts applied electromotive force failed to send a current through it, the galvanometer in circuit being capable of indicating 0.07 micro-ampere. This was tried repeatedly, the connections being tested so as to make

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certain that the resistance was surely in the tube. On breaking the seal at one end, current immediately began to flow from 0.3 volt upwards, and gas was visible on the cathode at 1.6 volts.

ELECTROLYSIS OF PURE WATER.

Distilled water was boiled in a platinum dish, and then placed between two platinum electrodes. The galvanometer in circuit was sensitive to 0.07 micro-ampere. No observable current passed, using up to three volts potential. With 1 volt potential across the electrodes, mixed oxyhydrogen gas was bubbled in midway between the two electrodes. A current immediately passed, equal to several micro-amperes.

CRITICAL VOLTAGE.

I. Heat Value of Decomposition.—A calorimetric experiment was made, electrolyzing dilute sulphuric acid with free disengagement of gases. Assuming 0.239 gram-calorie per second as the heat value of 1 watt, the heat obtained in the electrolyte corresponded to $C \times (V - 1.50)$. Or, in other words, the heat absorbed in chemical work corresponded to $C \times 1.50$, thus proving the energy absorbed in decomposing the water as 1.5 volts.

In detail the experiment was as follows: A water voltameter designed for the separate production of the gases was connected through resistance to an ordinary lighting circuit. 133 grams of 20 per cent. sulphuric acid at the temperature of the room was placed in it, the current was turned on and readings taken, at stated intervals, of the voltage, current and temperature. Below are the results and calculations.

Voltage absorbed by the cell ..... 18.1 volts.
Current ..... 0.51 ampere

Time in minutes.	Temp.
0	22.3°
0.5	22.8
1.0	23.3
1.5	24.0
2.0	24.5

Total time, 120 seconds. Rise, 2.20
Rise per second, 0.0183°.

Specific heat of 20 per cent. sulphuric acid 0.83
Heat received by cell per second, $133 \times 0.0183 \times 0.83 = 2.021$ gram-calories.

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Heat value of the current in calories per second $18.1 \times 0.51 \times 0.239 = 2.206$.

Heat absorbed in decomposition, $2.206 - 2.021 = 0.185$ gram-calories.

Voltage absorbed in decomposition, $\frac{0.185}{0.51 \times 0.239} = 1.51$ volts.

No corrections were made for the sensible heat of the evolved gases, or the losses by radiation. The sensible heat in the evolved gases was negligible in comparison with the heat capacity of the electrolyte. As to loss by radiation, the difference in temperature between the electrolyte and the external air was so small, and the time so short, that it was also considered negligible.

II. Critical Voltage by Measuring Counter-electromotive Force.—In the course of our experiments we happened upon this method of determining the critical voltage. We were using a cell 8.75 meters long (Fig. 2) with a resistance of about 10,000 ohms, and were constructing a current curve as will be described later. The cell was connected in series with a galvanometer and a 66-element Gülcher thermopile. The thermopile was lighted and simultaneous readings were taken of the current and the electromotive force. The electrodes used were small pieces of gold foil, and the electrolyte was dilute sulphuric acid of 10 per cent. strength. After reaching a maximum of 3.5 volts, the gas was turned off from the thermopile and it was allowed to cool. Simultaneous readings were again taken of the current and the applied voltage as before. As the thermopile cooled, the current dropped steadily and when the voltage had reached 1.5 exactly the current passing reached zero.

The same experiment was again repeated with platinum electrodes, and while the current did not drop quite as regularly as with the gold electrodes, still there was no doubt of the cessation of the current at 1.5 volts. The electrodes should be allowed to evolve gases freely for some time to give constant results in this class of work. If this precaution is taken, platinum electrodes give no trouble, and compare favorably with gold.

III. Critical Voltage as Determined by Observing Gas under the Microscope.—Two platinum electrodes, which had been running some time evolving hydrogen and oxygen, were immersed in a normal solution of sulphuric acid and placed under a microscope, magnifying 100 diameters. On applying 1.8 volts, gas was

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generated freely at the cathode and the anode. On cutting off the current the gas bubbles grew smaller until they finally disappeared. This was repeated with the cathode in the field at 1.75, 1.70, 1.65, 1.60, 1.55 and 1.50 volts. At the latter voltage a distinct gas bubble appeared on first closing the circuit, and then gradually decreased in size until it finally disappeared. At 1.45 volts, no gas bubbles appeared; at 1.50, they were again produced as before, on closing the circuit.

IV. Critical Voltage as Determined by Increase of Current with Increase of Voltage.—The current curve, by which is meant the curve obtained by plotting current as ordinates and voltage as abcissas, was found to vary greatly with the distance apart of the electrodes. Also the nature of the electrolyte affects the curve to a great extent. Yet even with these variations it might be expected that a decided break should occur somewhere at about 1.5 volts. With this end in view we conducted the following experiments and plotted the accompanying curves. It should be here stated that these experiments were not undertaken solely with this end in view, but rather for the purpose of gaining a better understanding of the phenomena of the residual currents which pass through such a dilute solution of sulphuric acid.

Experiment 1.—A cell was constructed of ⅜-inch glass tubing, using for electrodes two platinum wires having their ends 5 mm. apart. The electrolyte was 0.1 per cent. sulphuric acid. A varying voltage was obtained by changing the number of couples of a Gülcher thermopile, in circuit. The current was interrupted during the changing, and after closing the circuit, readings were taken every five seconds up to, in some cases, thirty seconds.

There were several kinks in the current curve, the only one with which we will concern ourselves at present being at about 1.45 volts, where a very decided rise took place, marking an increase in current.

Experiment 2.—The same experiment was repeated, using the same cell with the electrodes 5 cm. apart. The current curve for this cell shows an abrupt rise beginning at about 1.2 volts, instead of 1.5 as before, showing that the distance apart of the electrodes seems to affect the nature of the curve.

Experiment 3.—We tried the same experiment with extreme distance apart of the electrodes. In one case the electrodes con-

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sisted of platinum wires 8.75 meters apart, in the cell shown diagrammatically in Fig. 2. With an electrolyte consisting of 0.1 per cent. sulphuric acid, the curve (marked Exp. I (*a*) Plate I) is a perfectly straight line with no kinks or breaks in its entire length. Being only concerned with this point, we will not discuss at present its other peculiarities. The experiment was repeated with an electrolyte containing 10 per cent. sulphuric acid. Here

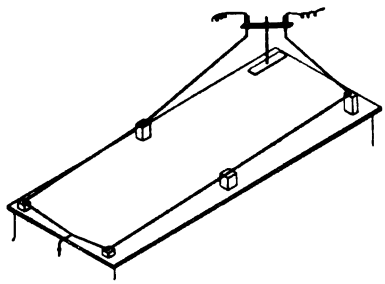

FIG. 2.

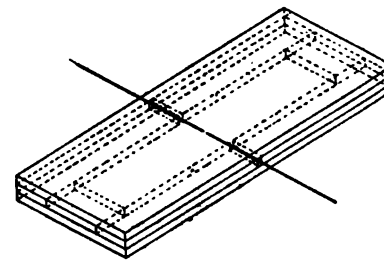

FIG. 3.

the curve rises somewhat steeply from the very beginning, with only a slight break at 2 volts.

Going to the other extreme, we employed a cell constructed as in Fig. 3, of glass, so that it could be used under the microscope. It consists of two microscope slides separated by pieces of glass, so as to leave a space in the middle for the reception of the electrolyte. By means of a scale in the eye-piece of the microscope the distance of the electrodes apart could be very accurately measured. We placed them $\frac{1}{8}$ of a millimeter in this case, and first used 0.1 per cent. sulphuric acid for electrolyte. We found on this curve (see Plate I) two distinct inflections, one at 2 volts and the other at 2.35 volts. On repeating the experiment with 10 per cent. sulphuric acid electrolyte, the curve showed only one inflection at about 1.7 volts.

These experiments showed the existence of many unexpected conditions affecting the presence or absence in position of the points of inflection of the current curve. The distance apart of the electrodes, the strength of the electrolyte, and the time interval between the opening and the closing of the switch in the circuit all seemed to have a marked influence on the nature of the curve. On the whole this seems to be a very unsatisfactory method of obtain-

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ing the critical voltage of an electrolyte. Method II is much more satisfactory.

RESIDUAL CURRENTS.

It has been known ever since the time of Helmholtz, that a current could be sent through an electrolyte, using insoluble electrodes at an applied voltage below that required for decomposition. We have already reviewed some of the work which has been done towards an explanation of this phenomenon, and it is now our purpose to discuss some of the results, and interpret them in the light of some of our own experiments.

Danneel, as has been previously stated, ascribed these small currents to the carrying capacity of the dissolved gases, oxygen and hydrogen, in his electrolyte, dilute sulphuric acid. Taking for instance the dissolved hydrogen he attempted to prove that the free ions took a certain charge from the cathode and by diffusion carried it over to the anode where a certain positive charge was neutralized when they came in contact with the anode. He made a calculation of the current which should thus flow through his cell and found a great discrepancy between his calculated and observed values.

Bigelow also made an extensive study of these residual currents his work being mainly a quantitative determination of them. His investigations covered a period of some eighty days, during which time he took readings at stated intervals, the results of which are carefully tabulated in his original paper. The great value of his work lies in the fact that it proves the theory upon which Nernst based his calculations. Bigelow had to wait between seventy and eighty days before the current became constant. On recalculating these results theoretically, using Danneel's formula, we have found the calculated value of this diffusion current to be 0.105 micro-ampere, against the minimum 0.088 micro-ampere found by Bigelow.

It may be that Danneel's figures would have corresponded more nearly with his calculated values, if he had taken readings like Bigelow, for seventy or eighty days, until the values had become constant. Danneel gives the time in only one instance, where he waited four days to get a constant value, but still obtained results thirty to fifty times as great as calculated. Bigelow's four-day results are forty times as great as his minimum obtained in

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seventy-two days, so that if Danneel had taken that time to each of his measurements, with the tube 26 cm. long, he would probably have obtained a "beobachtet" corresponding to his "berechnet."

In thus confirming the diffusion formula we also confirm the application of Faraday's law to these diffusion currents because this law is embodied in the application of the diffusion formula. To keep the electrolyte so saturated that the required current will pass requires that an amount of gas be evolved proportional to that carried over to the other electrode. As to the exact condition of these gases, we have come to the conclusion that they are in solution in the electrolyte, and that their recombination furnishes the energy which was absorbed in the decomposition, thus causing no absorption of voltage.

These diffusion currents are no doubt very constant in their value and must therefore be quite independent of the comparatively large current which flows on first closing the switch, and gradually falls off in value for as much as eighty-two days, as observed by Bigelow. These currents are undoubtedly caused by the using-up of dissolved oxygen and hydrogen in the electrolyte. The electrolyte carries the current, just as it does above the critical voltage, and with an internal friction according to Ohm's Law, but the amount of such current which can flow is conditioned not by the voltage applied but by the rate at which dissolved hydrogen and oxygen can get to the electrodes and combine with the hydrogen and oxygen which may be there set free.

In support of this statement we shall again refer to an experiment of ours, which has been cited before. Two platinum wires $\frac{1}{8}$ mm. in diameter were used as electrodes, heated to redness, and plunged 2 cm. into the electrolyte. The electrolyte was 0.1 per cent. sulphuric acid, made with distilled water and not used before, so nearly free from dissolved oxygen and hydrogen. The distance apart of the electrodes was 875 cm., cross section of the electrolyte 0.2 square centimeter. The theoretical resistance was about 1,000,000 ohms. A diagrammatic sketch of the cell is shown in Fig. 2. The curve is shown in Plate I. The current passing increased linearly with the applied voltage, without any kinks, no evolution of gas took place at the electrodes, and the amount of current passing was equal to the applied voltage divided by the ohmic resistance, within the errors of observation and cal-

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culation. But we cannot ascribe the whole of this current to true diffusion. The calculated diffusion current according to Danneel would be 0.0012 micro-ampere, whereas our lowest reading, at 0.3 volt, was 0.4 micro-ampere. With this long cell the limit which the current can reach is no doubt that set by Ohm's Law, because we have here gas enough in solution, aided by the diffusion current, to take care of all the current which this law would allow to pass.

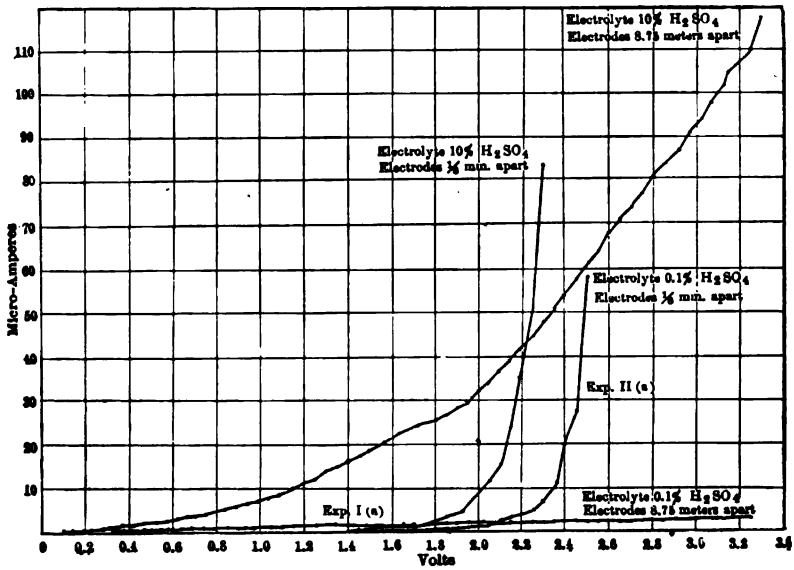

PLATE I.

Now as to the other case, that in which Ohm's Law will allow more current to pass than the dissolved gases and diffusion current can take care of, we have an example in the next experiment. The same platinum wires were placed as electrodes in the same kind of solution, with their ends ⅛ mm. apart, but with the active surfaces averaging virtually 2 cm. apart, the resistance (theoretical) was about 2300 ohms. The curve is shown also in Plate I. It will be noticed that no current passes until a voltage of 1.5 is reached, from that to 2.1 volts a smaller current than with the electrodes 875 cm. apart, from thence to 2.5 volts a rapidly increasing current with evolution of hydrogen at 2.4 volts, when the current flowing had reached 20 micro-amperes. In no case with

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the voltage used was the current more than a small fraction of that which would be calculated from $A = \frac{V}{R}$. The current showed a very slight rise at 1.8 volts.

The cell used in this case is shown in Fig. 3. It does not contain over a half cubic centimeter of electrolyte, and so can contain but a very small amount of dissolved gas. As the diffusion current is a very small factor also we can easily see here that the total carrying capacity of these two agencies are the factors which here condition the current, and not Ohm's Law.

Returning again to the comparatively large currents due to the gases already in solution going to the electrodes and combining with the products of electrolysis, thus permitting a current to flow through the electrolyte, we must be careful not to confuse them with the true diffusion currents. For want of a better term we might call them extra residual currents in distinction to the very small normal residual current.

The extra residual current starts with a certain maximum value which falls off with the time, and as Mr. Bigelow found reached a constant between seventy and eighty days. The explanation of this phenomenon which we have to offer is as follows. These currents are due as before stated to the combination of the dissolved oxygen and hydrogen in the solution with the nascent products of electrolysis. This combination taking place at the electrodes, no voltage is absorbed, and still a current passes through the electrolyte. This combination can only take place at the electrodes. When the current is first turned on, the electrolyte just around the electrodes is well saturated with the gases which are immediately available for use. This causes the large initial currents. But as the solution becomes impoverished, the electrodes have to draw from a greater and greater distance, with the result that less and less gas reaches them in a given time and so causes the observed fall of current. When the gases in solution have all been combined with the products of decomposition, then we have the phenomenon of the true residual currents.

That this current also follows Faraday's Law was proven by some calculations made on Mr. Bigelow's results. In his experiment 1, for instance, a summation of the entire current passing through his cell, until the minimum—the diffusion current—was

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reached showed that the extra residual current, above the diffusion current, could have consumed 0.00008 gram of hydrogen, or its equivalent in hydrogen plus oxygen, in the time given. If the solution was 10 cc. in volume (estimated; not given by Bigelow) it could have contained, if saturated, 0.00002 gram of hydrogen and 0.00048 gram of oxygen, equivalent altogether to0.00008gram of hydrogen.

There thus appears to be no doubt that Faraday's Law applies to the "Rest-strom" and that this current is composed of two factors:

I. A residual diffusion current, which is constant and is sustained by the diffusion of hydrogen and oxygen from one pole to the other.

II. A constantly decreasing extra current caused by the using-up of the dissolved hydrogen and oxygen, and which falls off as the concentration of the gases in the solution decreases.

It being manifestly impossible to conduct a series of experiments involving a large number of measurements at different voltages, if each single reading is to take seventy days, we consider that future investigators may take it as proven that the residual diffusion current is always to be counted on, and that its value may be calculated with sufficient accurateness by Danneel's formula. The second factor agrees very well with calculations based on the constantly decreasing current, the amount of oxygen and hydrogen it will consume, and the actual amount present.

CONCLUSIONS.

1. We have no explanation of the action in the closed tube.

2. There is no doubt that the actual voltage absorbed in the decomposition of water into free oxygen and free hydrogen is very close to 1.5 volts.

3. Faraday's Law applies to all currents passing through electrolytes, whether above or below the voltage absorbed in ultimate decomposition.

4. Ohm's Law applies to all currents passing through electrolytes, *i. e.*, the current in passing will lose in friction an amount of energy $= C^2R$. C will be equal to $\frac{V}{R}$ only when R is so high that C is less than the amount of current which can be sustained

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by the secondary actions taking place at the electrodes, *i. e.*, solution of a soluble anode or depolarization by dissolved gases.

5. Thomson's Rule applies to the decomposition of water. The voltage absorbed in decomposition can be calculated from the first and last states of the electrochemical system.

6. Gases in solution in pure water make it conducting, like salts in solution. All the phenomena of residual currents so far observed are explainable by the presence of gases in solution, by gaseous diffusion, and recombination at the electrodes.

ELECTROMETALLURGICAL LABORATORY,
LEHIGH UNIVERSITY.

DISCUSSION.

MR. B. MACNUTT: Mr. Chairman, I would like to ask Dr. Richards if he consider that every term drops out of the energy equation except "RI^2" when the current is small?

DR. J. W. RICHARDS: When the current is extremely small the only thing that is necessary is to consider the amount of products of electrolysis which can be taken care of or neutralized by recombination at the electrodes. The energy for decomposing H_2O to H_2 and O does not enter into the question; the voltage of decomposition also does not enter into the question.

DR. H. S. CARHART: RI^2 represents it all.

MR. MACNUTT: In regard to the polarization, do you consider it negligible with a very small current? A few years ago I made some experiments with electrolytic cells, using an extremely small current, about 10^{-7} amperes, and measured the electromotive force with such current. The conclusions I drew from my experiments were that Ohm's Law did not apply in that case; that is to say, there was an electromotive force there which was not the product of the resistance and the current going through the cell and which did not become zero with a zero current, nor was it any simple function of the current. Did I understand you to say that Ohm's Law, in your experiment, did apply with a small current?

PRES. RICHARDS: It applies with very small currents when the resistance between the electrodes is so great that the voltage absorbed in frictional resistance in the electrolyte, as calculated by Ohm's Law, is greater than the depolarization which can take place

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by residual gases. It applied in our experiments only to the electrolyte 8¾ meters long and with a one-tenth per cent. solution of sulphuric acid.

MR. MACNUTT: That, of course, would mean that the factor RI is larger than anything else and the other becomes negligible.

PRES. RICHARDS: Yes.

MR. C. HERING: Do I understand that Prof. Richards used platinum in these experiments?

PRES. RICHARDS: Yes.

MR. HERING: It seems to me that the use of platinum complicates matters very much because there is a well-known tendency of platinum to absorb hydrogen and oxygen, combining with them and forming some sort of a chemical compound. Platinum is therefore, in my opinion, a very poor metal to use in any such work. On one occasion in connection with a liquid potentiometer, I had to use something which would not absorb oxygen and hydrogen and found that gold was quite satisfactory, while platinum was absolutely useless.

The test which Prof. Richards described with an absolutely closed vessel seems to me to be a very remarkable one, so remarkable that I should like to see it repeated a number of times. I understood that there was sulphuric acid in that solution, and that the highest voltage was only 3.5.

PRES. RICHARDS: Yes.

MR. HERING: It would be interesting to see at what voltage decomposition would start in that case. In the 8-meter test I understood the voltage was raised to only 3.5. Was there any evolution of gas, because that was above the decomposition voltage?

PRES. RICHARDS: No sign of gas.

MR. HERING: I did not hear Prof. Richards suggest that there may be actual decomposition and that the gases so formed might pass through the solution in suspension or solution to the other electrodes. I think he referred only to the gases that were originally in the solution. It seems to me that it is not impossible to suppose that gases might actually be formed even if there were none in the original solution and that they also might travel from one electrode to the other and therefore carry a current below the

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decomposition voltage, because the oxygen traveling from the anode to the cathode would depolarize the cathode and the hydrogen would depolarize the anode.

In that test in which the amount of heat generated was measured, I would like to ask whether allowance was also made for the heat that passes out in the gases, or whether only the heat remaining in the liquid was measured. It seems to me that the gases themselves would carry off quite an appreciable amount of heat.

PRES. RICHARDS: I would like to reply to Mr. Hering's point. I think there is a great deal more difficulty made about platinum electrodes than is necessary, because of their supposed ability to absorb hydrogen or oxygen. They have not an indefinite ability to absorb an indefinite amount, and if the platinum electrodes are used until they have become saturated with oxygen and hydrogen they are practically then unalterable electrodes; they can not indefinitely absorb hydrogen and oxygen. By taking electrodes that have been used until they have freely given off hydrogen and oxygen, I take it that they are then in condition to act as unalterable electrodes. Regarding the amount of heat in the gases evolved in our calorimetric experiment, the rise of temperature was so very small—I think 1° in one minute—that it was from the rate of rise that we calculated the rate of evolution of heat; and the heat in the gases as compared with the heat in the solution was, I think, entirely negligible.

DR. CARHART: Did you correct for radiation loss?

PRES. RICHARDS: No, not for radiation; because the total rise of temperature was so small that the rate of rise was perfectly uniform. The experiment is one which needs the rate of rise of temperature to be determined, because that is proportional to the rate at which heat is being evolved in the electrolyte, and with a rise of 0.1°, 0.2°, or 0.3° the rate of rise can be very accurately determined per minute, and the amount of heat radiated by the apparatus for a rise of 1° is practically negligible.

DR. CARHART: It is appreciable. You might have allowed for it by taking the rate of cooling.

PRES. RICHARDS: We determined the rate of cooling in another test, in which the temperature of the electrolyte was raised almost to boiling, and as the temperature sank asymptotally towards the

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temperature of the room the final rate was so very slow that a correction for this in our experiment was a needless refinement, amounting to only a small fraction of 1 per cent.

MR. C. J. REED: If neither the oxygen nor the hydrogen is liberated, how do you know that the water is decomposed? How do you know it is not the other substances which are decomposed originally?

PRES RICHARDS: We have been decomposing dilute sulphuric acid and have considered the decomposition as practically the decomposition of water. We did not enter into the question as to whether it was primary or secondary.

MR. REED: I referred to your statement that if something else were present to combine with the oxygen or hydrogen so that they do not appear, you say in that case it would not take 1½ volts. I thought you referred to depolarizing agents, such as chromic acid, at the cathode and to a reducing agent, such as metallic lead, metallic zinc or something of that kind at the anode. In a case of that kind we have no ebullition of either oxygen or hydrogen because, as I understand your statement, there would be a combination of oxygen and hydrogen with those depolarizing and reducing agents. I ask, how do you know that there is any decomposition of the water at all in those cases? How do you know it is not simply an electrolysis of those other chemicals, the depolarizing and reducing agents, which are present. In other words, how do you know it is not an oxidation of lead or zinc at the anode and reduction of the chromic acid at the cathode?

I would like to say that it seems to me platinum electrodes are the very worst metals that could be used for any experiment of this kind. If we can imagine an experiment with electrodes which, in the beginning consist, one of zinc and the other of copper, and which, as the electrolysis proceeds, gradually change the zinc electrode into copper, and the copper electrode into zinc, so that as a final result they are both reversed,—you could not then have much worse conditions than you have in starting with two platinum electrodes (which are similar) and finally stopping your experiment when one has combined with oxygen and the other with hydrogen. The trouble with any experiment of that kind is that you have got a continuously varying electrode; and consequently it seems to me

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any experiments performed in that way are of exceedingly doubtful value as settling this question of electromotive force. It is well known that platinum combines chemically with oxygen and also with hydrogen, forming chemical compounds which look exactly like the metal, but have very different chemical properties, for instance, platinum combines with electrolytic oxygen in the same proportion as that in which they combine to form platinum oxide, evolving also the same amount of heat and yet the compound has the same general appearance and most of the physical properties of metallic platinum. We know also that two such platinum plates, one charged with oxygen and the other hydrogen, will form a galvanic battery in acids and will act like a zinc plate and a peroxide plate and will give an electromotive force of over one volt.

Dr. Richards states that the so-called "residual current" is sustained by dissolved gases, agreeing with the conclusion of Dr. Bigelow.

It seems to me there is no proof of that statement in any of the experiments cited. Faraday found that with very minute currents there was no electrolysis or chemical change in any solution, unless the intensity or electromotive force exceeded a certain minimum for each solution. He found that for each substance there was a certain electromotive force, above which it would conduct the current with decomposition according to the law of electrochemical equivalents, but below which it conducted exactly like a metal, that is, without decomposition. That was one of his generalizations. In proof of this he arranged a potassium iodide cell in series with a number of other cells containing various solutions and passed a minute current through the series for several weeks. The amount of KI decomposed was proportional to the quantity of electricity transferred, but there was no decomposition in the other cells.

Dr. S. L. Bigelow: I have recently made a few experiments, using gold electrodes and the general character of the results is the same as with platinum electrodes, although the current quantity is much less, no doubt because there is less occlusion.

As to this other question, whether dissolved gases really conduct or not, it has been suggested that they act simply as depolarizers,

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uniting with what is separated at the electrodes. I have carried out experiments as nearly identical as possible, excepting that in one my electrolyte was $^1/_{200}$ normal sulphuric acid and in the other was normal sulphuric acid; in other words, I increased the concentration of the acid 200 times, and yet observed practically the same current strength. If the dissolved gases act merely as depolarizing agents it seems to me that such a great increase in the concentration of the ions, while the amount of dissolved gas remains about the same, should be accompanied by a marked increase in the current. This is evidence, as far as it goes, in favor of the view that dissolved gases conduct as such.

DR. W. D. BANCROFT: In the remark of Dr. Richards on Ohm's Law it would have been much better to have said those experiments showed that the ratio of the counter-electromotive force of polarization to the applied potential difference approached zero as the resistance of the solution became very large. It seems to me that that is what has been actually found and that that is another way to put it than to speak of the applicability and inapplicability of Ohm's Law.

As regards the platinum electrodes it seems to me that we can hardly speak of a platinum electrode as being a definite unalterable electrode after a little hydrogen has been set free, since Bose's measurements showed that the potential of the platinum electrode is still changing after hydrogen has been bubbled over it for two weeks. Lastly, I think the experiments are hardly accurate enough to justify us in saying that Thomson's Law holds exactly, in view of the evidence that we have against the accuracy of Thomson's Law.

PROF. C. F. BURGESS: Some results which Dr. Richards has described can be exaggerated if the process is carried on under very high pressures. I carried out, at one time, some experimental work which seems to have a bearing along this line; a steel cylinder into which one electrode was fixed by means of hard rubber was filled almost completely with a solution of sodium hydroxide, the cylinder constituting the other electrode. By passing a current through this cell, a pressure was developed which was estimated to be over 1,000 pounds per square inch. Measurements were made with an ammeter and it was found that a current could be made to flow at

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a pressure considerably below one volt. I assume that the reason for this was that the high pressure of the gases caused an increase in the solubility and therefore acted as a more efficient depolarizer than under atmospheric pressure. I also obtained an effect which is similar to that which was described in connection with the enclosed thermometer tube. After a high pressure had been developed in the above apparatus, increasing the amount of current for a short time, it was found that the pressure necessary to force the current through rapidly increased to such a degree that a pressure as high as 60 or 70 volts could be applied and even then very little current would flow, as indicated by the ammeter. While not having sufficient data to explain this phenomenon, one of the suppositions which presented itself was that a layer of gas surrounded one of the electrodes and thereby insulated it, and that it was due to the high pressure that the gas layer was not destroyed. It was also noted that by shaking the cell the current would again flow for a short time and would then become interrupted. A measurement of the polarization at the time of the application of the 60 volts pressure showed that it was, as I remember it, something less than 1 volt.

MR. HERING: In that experiment it might have aided in explaining the result if Prof. Burgess had reversed the current at the time when he found he could get no more current through the cell; this would have depolarized both electrodes.

MR. H. E. HEATH: I would like to put Dr. Richards' information in a little different form. He has said that we get the decomposition of water at a voltage of less than 1.49. I do not think that he means exactly that. What he means is that we get this decomposition with an external voltage of less than 1.49, the idea being that we get a recombination or a counter-electromotive force in the solution itself, which causes an external voltage of merely the difference between the two.

MR. W. S. LANDIS: I would like to ask Mr. Burgess whether, taking a small thermometer tube such as we use (probably about an inch and a half long) there would be any appreciable advantage in shaking it if it was absolutely full of liquid. Our platinum wires very accurately fitted the bore of the tube; placing the tube under the microscope we could barely see any space between them

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and the walls. By filling the end, the balsam was cooled and was drawn into the tube by capillary action, leaving practically no space we could see under the microscope. Would there be any appreciable effect in shaking that tube, considering the fact that the space was entirely filled with electrolyte?

MR. REED: I could not repeat that experiment with a closed tube because I was unable to get the tube sealed up that way. I found great difficulty, after getting in the wires and getting it full of acid, in getting any balsam or any other kind of cement that would actually fill the remaining space and keep it perfectly dry on the end so that I could be sure there was no leakage. I would ask Dr. Richards how he was sure there was no leakage and how he constructed that apparatus. I should like to be able to repeat that experiment, but confess that I was unable to do it.

MR. A. H. COWLES: Did you make an observation immediately at the beginning of the experiment, to note if there was not at first an impulse or flow of current followed by a falling off of the same, for there might have been a current for a few moments which fell off, and after that the leakage might not have been found?

MR. LANDIS: The instrument we used for measuring these small currents was a millivolt meter, reading, I believe, to about three-hundredths of a millivolt, with a resistance of 139 ohms, and in series with our cell. That would allow us to read two- or three-tenths of a micro-ampere. There was no appreciable motion of the needle in that instance. Of course, with a much finer galvanometer, reading more sensitively the current may have been of some appreciable value, but with our instrument there was no current shown.

PRES. RICHARDS: Mr. Landis is my assistant, who has made the experiments with me. The instrument we used would show at the closest reading a fraction of a micro-ampere—nearly, you can say, one-tenth of a micro-ampere at its highest delicacy; there was no appreciable motion of the needle at the beginning.

Replying to Mr. Reed, the tube was part of a very delicate thermometer that has been broken, and with a very fine bore and thick walls—which we selected, as I explained, in order that it would not be possible to break it. The tube was filled with electrolyte from one end to the other, the wires were inserted to within one

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millimeter of each other, and then, the wires being bent over so as to be out of the way, liquid Canada balsam was dropped on the end of the tube and allowed to set. There was no empty space between the liquid and the balsam when the tube was sealed; under those conditions no current passed when over 3 volts was placed on it. On breaking the seal the current immediately passed.

MR. REED: How did you ascertain that there was none of the acid on the end of the tube under the balsam? You could not prevent the capillary attraction from causing the acid to follow the wire and thus get out over the end of the tube. I found it was impossible to get a seal that could be relied on as being perfect. Of course you might easily have it sealed so that you could not see any defect with the naked eye. I could not satisfy myself that there was no defect. I would also ask how you held the balsam against this enormous pressure which you subjected it to. How, in other words, did you know that there was not an expansion there that forced the balsam out a little at the end so as to relieve the pressure.

PRES. RICHARDS: I did not know many of those things. We observed no liquid oozing out at the end of the tube.

MR. REED: You would not expect to observe it from the amount of gas which would be formed by the minute current that you could not measure during the first instant.

PRES. RICHARDS: We observed no gases set free on the electrodes and we were able to get no current through. If there had been leakage we would have got the current through as we did every time that our tube leaked, which happened with some of the thermometer bulbs. Every time that the places, where it was closed, leaked we had no difficulty in getting the residual current through.

MR. REED: What test did you apply to see whether the tube leaked before you applied the current? Or was the current the test—the fact that you got current through, or did not? If that is so, then you are taking the thing proved as the proof.

PRES. RICHARDS: We used a piece of blue litmus paper and a hand lens, and carefully touched the end of the tube to see if there was any sign of acid. With capillary tubes that we had sealed we found considerable difficulty in getting a tight seal. Only one tube remained tight after the attempt to pass the current through it.

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MR. COWLES: My question was directed to the point that at high pressure, say a thousand atmospheres, the quantity of gases a solvent will absorb should be a thousandfold greater than would be the case at one atmosphere pressure, and therefore there would be quite a little period, while the gases were being evolved and while they were going into solution, during and following which the pressure would be building up, and it seems to me that, during that period, or at the beginning of it at least, you ought to be able to get some observable reading from your milli-ampere meter indicating a current flow. After the pressure has built up it may act as a factor, reinforcing chemical affinity, and thus cause the stability of the water molecules to become so great that the electric force that is trying to break them down may not be sufficient, thus causing a stoppage of the process of electrolysis, and consequently of the flow of current. During the time that the pressure is raising in the tube, it seems to me that you ought to be able to note the beginning of the flow of a current, and then see it stop.

MR. LANDIS: In one experiment we used the drawn-out glass tube shown in the upper part of Fig. 1. of our drawings. It had a bulb at one end into which the two very fine platinum wires were sealed, and was drawn out to a capillary tube (possibly the size of the bore of the thermometer) and filled with liquid and sealed. Of course in sealing this end it left a small space, practically a vacuum. To fill that up all we had to do was simply to heat the tube, which expanded the liquid in the tube and filled it up completely to the top. It was placed on a 110-volt circuit. It is the only one all of glass that we sealed up successfully. The wires were probably 2 millimeters apart, very fine, and I suppose had a resistance of practically 10 ohms. There was also in series a 220-ohm lamp. Placed in a 110-volt circuit the tube broke; but the instrument, as I remember it, registered about 7 millivolts (equivalent to about 50 micro-amperes) and rapidly fell off until the tube broke—the whole thing exploded in twenty seconds after the current was put on and the glass was literally pulverized.

MR. REED: This shows, does it not, that the statement of Mr. Cowles was correct?

MR. LANDIS: There is a certain current going through the tube.

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That is not an exactly similar bulb to the other one on account of the bore not being capillary, and the walls being somewhat elastic, whereas the other tube, I should say, did not permit of any great amount of elasticity.

MR. COWLES: I think it must be true that there were gases evolved at the beginning of the experiment at the two poles. It would take some little time for the full pressure to develop itself to its maximum amount throughout the thermometer bore. The act of diffusion of gases through a liquid is a slow process, and it may be that the time necessary for diffusion would be a factor that should be considered.

MR. REED: There are some statements and facts that I am unable to reconcile. In one experiment it is shown that current does pass at the initial stage. In the experiment of Prof. Burgess it is shown that after the pressure has been increased the current will still pass and at a lower voltage. The experiment which Mr. Hering and myself performed some years ago, and which Mr. Hering described at the last meeting, showed that as the pressure increased the voltage required to decompose water diminished. Now, according to these experiments, current will pass during the first instant and then cease, as the pressure rises. But, according to the experiments of Prof. Burgess, and those of Mr. Hering and myself, an increase in the pressure causes the current to flow at a lower electromotive force. I am not able to reconcile these results.

MR. COWLES: In your experiment you had a large volume of water and electrodes rather close, and I think there was a more ample chance for diffusion.

MR. REED: They were not as close together as in this case.

MR. COWLES: You had the ends of the two wires rather close together in the thermometer tube. You had a very small cross-section for the lateral diffusion of the gases evolved.

MR. REED: Our wires were farther apart than in this case. They were several millimeters apart in our experiment.

MR. HERING: At least 1 millimeter.

MR. REED: At least 1 millimeter, and the volume of liquid experimented on was very small, possibly not greater than in the case of the bulb in this case.

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MR. COWLES: Was it greater than in the case of the narrow bore of the thermometer tube that Mr. Richards required?

PRES. RICHARDS: I think that the elasticity of the containing vessel explains the small current passing at first, since in the case of this thermometer bulb which Mr. Landis has spoken of there is a certain amount of elasticity of the walls which will allow of some expansion. In the small-bore thermometer tube with which we experimented, the expansion due to elasticity is, I think, negligible. With walls of the tube 2 millimeters thick and the bore only 0.25 millimeter, I think elasticity of the tube and the possibility of breaking it may be left out of consideration, whereas with the bulb the walls of the tube were certainly elastic, and after twenty seconds the elastic limit was passed and the tube was shattered.

MR. P. G. SALOM: What electromotive force was put on that?

PRES. RICHARDS: 110 volts.

MR. SALOM: Did you try lower voltages first?

MR. LANDIS: We tried the high one first to see if it was tight.

MR. HERING: It seems to me that Prof. Burgess' experiment in which he got no further current explains the experiment described by Prof. Richards, who also obtained no current. In Prof. Richards' experiment the amount of liquid was so small that the conditions of very great pressure was probably produced instantly, before he could even take a reading of his instrument.

MR. MOTT: I would like to ask Prof. Richards as to his conclusions concerning Ohm's Law. If a 0.2 per cent. sulphuric acid solution had been used instead of a 0.1 per cent. sulphuric acid solution would the conductivity have been doubled? In other words, does the sulphuric acid or the dissolved gases do the conducting?

PRES. RICHARDS: That was one of the experiments we might have tried. We filled our long tube (8¾ meters long) with a 10 per cent. solution of sulphuric acid for our next experiment and found that the current was not proportional to Ohm's Law. We made no intermediate experiment. I would like very much to make others, and hope, as soon as we have opportunity, to repeat some of those experiments with a strong acid and also very great resistance, to see if we do get current in that case proportional to Ohm's

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Law, when the gases present in the solution are able to take care of all the current which flows.

PRES. RICHARDS (Communicated): Mr. Landis and I have since tried Mr. Mott's suggestion of using differing strengths of dilute acid in our long tube, and find our first conclusion confirmed. The feeble currents flowing through these great resistances are proportional to the strength of the acid, and, in any one case, to the voltage applied. This has been found to be the case with our long tube for acids from 0.2 per cent. to 0.01 per cent. and for voltages from 0.1 to 110.

We feel more persuaded than ever that when the current which can flow through the electrolyte by Ohm's Law $\left(C = \frac{V}{R}\right)$ is *smaller* than the gases in solution can simultaneously take care of by depolarization, that then $C = \frac{V}{R}$ is the law applying to the passage of electric current through the electrolyte. When, however, the voltage is so high or the resistance so low that C calculated as $\frac{V}{R}$ is too large to be thus taken care of by depolarization, then the capability of the dissolved gases to get to the electrodes and perform the depolarization sets a limit upon the amount of current which can pass without expending the energy of decomposition. When this point is reached decomposition in its true sense begins, that is, some of the energy of the current begins to be applied to decomposing the electrolyte without simultaneous recombination or depolarization at the electrodes.

To make this clear, let C′ be a current passing at voltage V′ (the Ohmic resistance being R), and assume that C′ is smaller than should flow by the law $C' = \frac{V'}{R}$. This is the case where, according to our view of the matter, the current is limited below $\frac{V'}{R}$ because the dissolved gases are not able to perform perfect depolarization. In this case the total energy of the current is $E = C'V'$. Of this, an amount equal to C'^2R is necessarily absorbed in overcoming Ohmic resistance, leaving $C'V' - C'^2R$ excess energy to be accounted for. This excess energy is applied to *ultimate decom-*

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position of the electrolyte, and will *liberate* oxygen and hydrogen at the electrodes in amount corresponding to $C'' = \frac{C'V' - C''R}{1.5}$, so that Thomson's rule is satisfied, as well as Faraday's.

When C″ is small the liberated gases may all go into solution, and thus reciprocally increase the amount of depolarization possible. When C″ is so large that the liberated gases cannot all get into solution they will become visible. *This* may occur at applied voltages much below 1.5 or may not occur until 100 volts are applied, according to the size of the electrodes, distance apart, resistance of electrolyte, nature of the electrolyte and its temperature.

LEHIGH UNIVERSITY,
May 16, 1903.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

EXPERIMENTS WITH METALLIC DIAPHRAGMS.

By Wilder D. Bancroft.

With an interposed metallic diaphragm we can have anything between the two extremes in which all, or practically all, of the current passes through the diaphragm and in which practically none of the current so passes. Instances of the first type are the mercury diaphragm in the Castner soda process and the copper electrodes in the Hayden system of copper refining as practised at Baltimore. Instances of the second type are the iron gauze diaphragms in the Castner sodium process and the Siemens-Halske process for hydrogen and oxygen. The condition for the whole current passing through the diaphragm is that the diaphragm shall fill completely the cross-section of the electrolyte. When the diaphragm does not fill the cross-section completely, the percentage of the total current passing through the diaphragm depends on the surface, thickness and nature of the diaphragm, on the nature of the electrolyte, and on the fall of potential in the electrolyte.

When the diaphragm fills the cross-section completely, the excess voltage necessary to pass a given current will be zero if the diaphragm is a completely reversible electrode and will be equal to the polarization value, or decomposition voltage under the circumstances, if the electrode is not attacked. In so far as the electrode is only partially reversible, intermediate values will be obtained, the excess voltage falling short of the decomposition voltage by the amount of depolarization which takes place. If we consider a mercury diaphragm between two caustic soda solutions of the same concentration there is no excess voltage due to polarization so long as the concentrations of the sodium amalgam are the same at the two surfaces. If this is not the case or if there is metallic connection between the diaphragm and the cathode, the depolarization is not complete.

The case where the diaphragm does not divide the electrolyte into two detached compartments has been studied by Löb and

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Kauffmann,[1] by Kauffmann,[2] and, quite recently, by Brochet and Barillet.[3] Stated briefly, no current will flow through a metallic diaphragm unless this require a lesser expenditure of energy than to make the current flow through the electrolyte. Since the resistance of a metal plate is practically always less than the resistance of an equal thickness of electrolyte, current will always pass through an interposed plate unless prevented by polarization. If the thickness of the interposed plate be sufficiently great, the fall of potential in the plate plus the polarization may be made less than the fall of potential in the liquid, and current will then pass through the diaphragm. If we place a thin platinum plate in a copper sulphate solution between copper electrodes, there will ordinarily be no precipitation of copper upon it, because it would take an enormous current to give the necessary fall of potential in a layer of electrolyte equal in thickness to the platinum plate. If we place a copper plate of the same thickness in the solution, current will flow through it, depositing copper on one side and dissolving it from the other. This can be shown very well by coating a platinum electrode on one side with copper and placing it in the solution with the platinum side facing the anode. This side becomes coated with copper while the copper dissolves from the side towards the cathode.

Experiments were next made with a thick carbon plate interposed, in order to find the exact conditions, under which there is precipitation of copper. When the fall of potential between the ends of the carbon electrode, as measured on copper wires dipped in the electrolyte, is less than one volt, there is no precipitation of copper. When the fall of potential exceeds 1.4 volts, there is a rapid precipitation of copper on the end of the carbon plate nearest the copper anode. On passing a current for a long time, there was a slight deposit of copper even when the difference of potential was only 1.1 volts. As the electrolyte was normal copper sulphate, this is below the decomposition voltage. It was thought at first that this might be due to an action of oxygen at the anode end of the carbon plate. Subsequent experiments with platinum electrodes led to another explanation.

In order to avoid having to use platinum electrodes of great thickness, experiments were made with two movable platinum

[1] Ztschr. Elektrochemie, **2**, 341 (1896)
[2] *Ibid.*, **3**, 237 (1896).
[3] Comptes rendus, **135**, 854 (1902).

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electrodes connected metallically outside the solution. It was expected that this would be equivalent to a massive platinum bar but this proved not to be the case. Instead of one electrode being anode and the other cathode, each electrode behaved to a certain extent both as anode and as cathode. This will be clear from

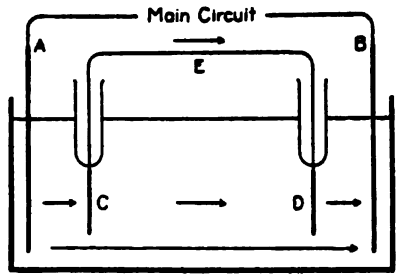

Fig. 1, in which A and B are the copper electrodes, C and D the interposed platinum electrodes, and E the metallic connection between C and D. The electrolyte is normal copper sulphate. Part of the current flows through the solution from A to B, as shown by the long arrow. If the potential difference between C and D be sufficient, some current will pass from A to C and from D to B. Part of this current will flow through the solution from C to D and another part through the metallic circuit C E D.

The existence of the current passing through the solution from one electrode to the other can be shown in various ways. A voltmeter placed across the terminals of the platinum electrodes does not show the true fall of potential in the solution; but only the difference between that and the counter-electromotive force of polarization at the electrodes. If the main circuit is broken, there is a current in the direction C D E C. If the side of the platinum electrode C away from A be covered with copper, this copper will gradually dissolve while copper is precipitating on the other face and an ammeter shows a current flowing through C E D. There is therefore a copper polarization at C and D, and also a copper depolarization at the same electrodes. The copper depolarization is the same as an oxygen polarization. If the two were exactly equal, the two electrodes would apparently be at the same potential as shown by a voltmeter, and no copper would be precipitated.

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If the two differ by any amount, the voltmeter will show a difference of potential and there will be a precipitation of copper on electrode C. This has been observed with an apparent potential difference of 0.1 volt as shown by the voltmeter. This value of 0.1 volt is not to be considered as an actual limit but merely as the lowest value at which I have experimented.

The true potential difference between the electrodes can be determined with an approach to accuracy by measurements on copper wires placed temporarily close to the platinum electrodes. Under these circumstances we should expect to find that the difference of potential necessary to precipitate copper on one of the platinum electrodes should be less than the decomposition voltage for copper sulphate, owing to the depolarization. This is analogous to the lowering of the voltage necessary to decompose water in the recent experiments of Hering.[1]

In my experiments platinum electrodes, 2 sq. cm. on a side were used and these were placed as close as possible to the copper electrodes A and B, so that the fall of potential between the two ends of the solution should not differ by much from the potential difference between the platinum electrodes. When this latter value is about a volt, a perceptible amount of copper is precipitated in a few minutes; when this value is about 0.7 volt, there is a visible deposit of copper in two to three hours; when the value is 0.5 volt, there is no sign of a copper deposit at the end of eighteen hours. Further experiments will be necessary to determine in how far this apparent limit varies with the size and shape of the interposed electrodes and with their distance apart. The point that has interested me has been the existence of the depolarization phenomenon and the consequent precipitation of copper under differences of potential far below the normal decomposition voltage for the solution. It is important that the exact conditions be determined under which decomposition takes place with the minimum voltage, in order to avoid those conditions, for instance, in the electrolytic generation of hydrogen and oxygen when using an iron gauze diaphragm.

[1] Trans. Am. Electrochemical Soc., 2, 139 (1902).

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

THERMO-ELECTROMOTIVE FORCE WITHOUT DIFFERENCE OF TEMPERATURE.

By Henry S. Carhart, LL.D.

In my investigations relating to the rôle of thermo-electromotive forces in a voltaic cell, I have applied them to the analysis of the temperature coefficient, to the localization of the absorption and generation of heat at the electrodes, to the variation of electromotive force with the concentration of the electrolytes, and to the electromotive force of a concentration cell. This view of the temperature coefficient, as the difference of the electrolytic thermo-electromotive forces per degree at the two electrodes, is sustained by the measurements in a most satisfactory manner, and it has been accepted in this country and in Europe by those most competent to judge.[1] So also the difference in heating at the electrodes when a current flows, I have shown mathematically to be an extension of the Gibbs-Helmholtz principle, and have confirmed the results by quantitative experiments.[2]

In the discussion following my last paper before the American Electrochemical Society, and in a recent issue of a German technical journal, the objection has been made to these applications, particularly as regards the concentration cell, that such thermo-electromotive forces come into play only when the junctions are at different temperatures. It is to this objection that I wish to direct attention in this paper.

The inquiry is naturally divided into two parts: first, the existence of thermo-electromotive forces without difference of temperature at the junctions; and, second, the resultant thermo-electromotive forces in a closed circuit.

The Peltier phenomenon is itself sufficient evidence that it is not necessary to heat a junction in order to excite there an electromotive force. In fact this phenomenon is but a single example of a

[1] Jaeger's "Die Normalelemente," p. 38; Cooper's "Primary Batteries," p. 53.
[2] "Physical Review," July, 1900, p. 1.

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very general law, namely, that when a current flows across any part of a conducting circuit, which is the seat of an electromotive force, energy is either given to the current or is taken from it, according as the electromotive force at the point is directed with the current or against it. Thus, in a direct current motor the current does work against the counter-electromotive force generated by the motor, and the product of the motor is mechanical motion. In a "booster," on the other hand, the generated electromotive force has the same direction as the current, and the current receives energy from the generator. Similar relations obtain in a storage battery. Now unless the devices employed are such that the work done by the current at the seat of an opposing electromotive force takes some other form of energy, the circuit is invariably heated. In the opposite case, the conductor gives up heat energy and cools. In a Daniell cell, for example, the thermo-electromotive force at either electrode is directed from the electrolyte to the metal. At the zinc, therefore, heat is generated, while at the copper it is absorbed, and the flow of current produces a difference of temperature between the electrolytes surrounding the electrodes. If a current is sent through the cell in the opposite direction, a similar temperature difference is established, but the absorption and generation of heat are then at the opposite electrodes. These temperature changes have nothing to do with the resistance of the cell, and they are proportional to the first power of the current. The direction of the thermo-electromotive force at a copper-iron junction at moderate temperatures is from copper to iron. In accordance then with the general law, when a current is sent across this junction from iron to copper, heat is generated and the junction is heated; if the current passes from copper to iron, heat is absorbed and the junction is cooled. The Peltier effect proves the presence of an electromotive force at the contact of dissimilar substances, and the value of this electromotive force is determined by the usual thermo-electric experiments. This statement is justified by the measurements made on the Daniell cell before alluded to. The following are the results:

Temperature difference between electrodes observed in a Daniell cell	0.165°
Temperature difference calculated from thermo-electromotive forces	0.160°

Helmholtz remarks in his celebrated memoir on "The Thermo-

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dynamics of Chemical Processes" as follows: "There are besides differences of heating at the two electrodes, which in their manner of appearance are similar to Peltier's phenomena in the case of thermo-electric currents, even though they are perhaps of different origin." The agreement between theory and observation now justifies the statement that they are the same in origin.

A very striking illustration of the general law under which all these facts range themselves, has been brought out by Duddell, in London, within the past year. He finds an electromotive force between carbon and carbon vapor, and it is directed from the latter to the former. When therefore the arc is formed, heat is generated at the positive carbon, where the current flows against this thermal electromotive force, and is absorbed at the negative carbon, where it flows in the same direction as the electromotive force there. We have thus an interesting explanation of the higher temperature of the positive carbon.

It is not open to question then that there exists an electromotive force at the junction of two dissimilar substances. The other question remains to be answered. We have been taught that the thermo-electromotive force integrated around a circuit, composed of two or more metals, vanishes when the whole circuit is at one temperature. This law is undoubtedly true for circuits wholly metallic. The denial of it would involve the absurdity of a self-acting thermo-electric engine, continuously converting the heat energy of the surroundings into the energy of an electric current, *without any change in the circuit which would limit the process.* It would be a kind of perpetual motion by which the kinetic energy of diffused heat might be converted into potential energy, or be made more available. The integrated electromotive force around such a circuit therefore vanishes, unless there are differences of temperature.

When the circuit is partly metallic and partly electrolytic, the case is quite different. Imagine a zinc rod bent in the form of a U, and let the two ends be immersed in a solution of zinc sulphate. If now one side of such a cell be slightly warmed, the warmer end of the rod becomes the positive electrode of a thermo-electric cell. Its electromotive force will be expressed by the equation

$$E = T\left(\frac{dE}{dT}\right)_p - T'\left(\frac{dE}{dT}\right)_n$$

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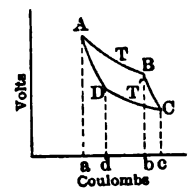
in which T and T′ are the temperatures in absolute degrees, of the positive and negative sides respectively of the cell, as denoted by the subscripts p and n. But the flow of current produces changes in the concentrations at the electrodes, with a resulting back electromotive force. If the equalization of concentrations by diffusion is prevented, the above expression finally becomes zero by the decrease of the thermo-electromotive force at the positive electrode, and its increase at the negative.

If two zinc rods joined, let us suppose, by a zinc wire as a resistance, are immersed in solutions of zinc sulphate of different concentrations, the combination is a concentration cell. The current through the cell is from the more dilute to the less dilute solution, and the flow of current acts to equalize the concentrations and reduce the electromotive force. Hence the device as a thermal engine is self-limiting. It can convert some of the equally diffused heat of its surroundings into electric energy, but it can not do so continuously, and can repeat the process only by having the cycle of operations reversed.

It may clear our conceptions of such a cell to carry it through a complete Carnot's cycle. Imagine the cell to be contained in a case impervious to heat except through the bottom. Let the porous partition separating the two solutions be a good conductor of heat, but preventing sensible admixture of the liquids. All parts of the cell may then remain at the same temperature. This cell is the working part of a Carnot engine, which includes in addition a conducting stand A at a temperature T, a non-conducting stand B, and a conducting stand C at a lower temperature T′. The usual cycle of four operations may now be carried out.

First.—Place the cell on A and let a small current flow till its electromotive force has fallen from the value denoted by the ordinate Aa in the adjoining figure, to that denoted by Bb, the



temperature remaining at the value T by absorption of heat from the stand A. The change in concentrations causes the decrease

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of electromotive force, and the cell works along the isotherm AB. Heat is absorbed because the thermo-electromotive force working with the current at the positive electrode is greater than the opposing thermo-electromotive force worked against at the negative. During this operation the work done by the cell is equal to the area AB*ba*. The co-ordinates are electromotive force and quantity of electricity.

Second.—Transfer the cell to the stand B and let the current flow till the electromotive force falls to the value C*c* and the temperature to T'. The cell then works along the adiabatic BC. Its temperature falls because the heat absorbed at the positive electrode is still somewhat greater than the heat generated at the negative. The internal resistance of the cell and the current are both supposed to be so small that the heat generated within the cell, proportional to the square of the current, vanishes, and quantities proportional to the first power of the current only are to be considered. In this second operation the electromotive force falls for two reasons, the change in the concentrations and the fall of temperature. The curve BC is therefore steeper than the curve AB. The work done by the cell during this second stage is represented BC*cb*.

Third—Transfer the cell to the stand C at the temperature T', and pass a reverse or charging current through it at the lower temperature and electromotive force, till the work done on the cell (not on its external circuit) along the lower isotherm CD equals the area CD*dc*. This work must be considered as negative. The cell gives out heat to the stand C, the reverse current augments the difference of concentrations, and the electromotive force rises.

Fourth.—Transfer the cell to the stand B again and continue to pass a charging current till the temperature of the cell rises to T. The opposing thermo-electromotive force is now greater than the direct, and heat is generated in the cell. Work done on the cell along this adiabatic DA is equal to the area DA*ad*.

The cell is completely reversible and has been brought back to initial conditions in all respects. It has the same internal energy, whether chemical or thermal, while the excess of work done by the cell during the entire cycle over the work done on the cell is denoted by the area ABCD. This energy is derived from the heat taken in during the first operation with the usual ratio for the efficiency of a reversible process. The cell works

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like any other thermodynamic engine, which is carried through a complete cycle of operations, taking in H units of heat at the higher temperature T, and giving out H' units at the lower temperature T'.

A concentration cell carried through such cycles may convert heat into electrical energy indefinitely. So may a steam engine and an electric generator. If the cell does not work in a cycle, its function is then limited to the first operation along the isotherm AB. Gas under pressure in a tank may do the same thing. An essential element is the presence of a stress. In the concentration cell this stress is the difference of the thermo-electromotive forces at the two electrodes. There is no question that there is such a difference, and it is not neutralized by a thermo-electromotive force between the two solutions.

A temperature coefficient is the difference of the thermo-electromotive forces per degree between the metal and the electrolyte at the two electrodes. Whenever a cell has a positive temperature coefficient, it absorbs heat and converts it into electric energy. A concentration cell has an electromotive force proportional to its absolute temperature. It also converts heat from its surroundings into electric energy. It does it by means of the fact that the thermo-electromotive force at the positive electrode is greater than that at the negative. Its electromotive force is therefore thermo-electric. If any part of its electromotive force is derived from internal energy, such as the heat of solution, the argument is in no way invalidated. To the extent that it takes in heat from its surroundings and converts it into electric energy, its electromotive force is purely thermo-electric.

It is obvious that any reversible voltaic cell, having a positive temperature coefficient, may be carried through such a cycle as I have described, and the area ABCD will represent the work done by absorbed heat in addition to the work done by the internal energy of the cell. The electric pressure, by means of which this heat energy is transformed, is denoted by the second term of the Helmholtz equation, expressing the electromotive force of a voltaic cell. This term is the integrated value of the thermo-electromotive forces in the circuit. Any voltaic cell with a positive temperature coefficient converts absorbed heat into electric energy; a concentration cell is an extreme type, which absorbs all. or nearly all, of its electrical output as heat.

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DISCUSSION.

THE CHAIRMAN: If there is no other discussion, I would like to ask Dr. Carhart a question. In a metallic circuit composed of, let us say, iron, copper and zinc, and forming a thermo-electric circuit, it is usual to assume that the algebraic sum of the thermo-electromotive forces in the circuit is zero. If we take a battery which consists of a partly metallic circuit and two solutions, of different concentrations, and assume a certain thermo-electromotive force of one solution against the metal and of the other solution against the metal, different from each other, have we any experimental or theoretical reason for not assuming that the electromotive force between the two solutions is equal to the difference of the electromotive forces of one solution to the metal on one side and the other solution to the same metal on the other side? Why should not the algebraic sum of the thermo-electromotive forces in this whole circuit be zero also? I think it is the usual thing to neglect the thermo-electromotive forces at the junction of the two solutions; or to say that it is negligible. Theoretically, if it is thermo-electric, why is not the thermo-electromotive force between the two solutions equal to the difference between that of the two solutions and the metal, the same as we would say that the thermo-electromotive force of copper to zinc is equal to the difference between the thermo-electromotive forces of zinc to iron and of copper to iron, in a metallic circuit?

MR. CARHART: Let me repeat one or two things that I said. Unquestionably, in an all-metallic circuit, the integrated thermo-electromotive forces around the circuit are zero if there are no differences of temperature. That does not mean that the electromotive force at each junction is zero, but only that the integrated or algebraic sum of the thermo-electromotive forces at the several junctions is zero. And the reason I gave is that if it were not so, we could have a device for the continuous conversion of heat energy into the energy of an electric current without anything in the circuit to limit its action, because there is no change taking place in the circuit. Take the other case, where we have junctions between electrolytes and metals; and in the case I supposed, we have only one metal, zinc. We know that those electromotive forces at the two sides are not equal to each other. The electromotive force at

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the junction of the two solutions has been measured and we cannot find any which is equal to the difference of the electromotive forces between the electrolyte and the metal on the two sides. In a Daniell cell I have attempted to find the electromotive force between nearly saturated solutions of copper sulphate on the one side and zinc sulphate on the other side and I have failed to find anything that I could measure with a wide range of temperature. I presume there is a small electromotive force there, but I have not been able to measure it. I can find the difference between the two sides with ease. We can say, therefore, that we cannot find a difference in the thermo-electromotive forces between two solutions, differing in density, which equalizes and offsets the difference of thermo-electromotive forces at the two electrodes. That is the first point.

I might answer the question by asking why we should expect the integrated value to be zero. We have no reason to expect it to be zero as far as I can see. In this case we have a cell which is self-limiting; there are changes taking place in the concentrations of the two solutions which equalize the concentration and so limit the action. It is running down along the isotherm AB.

MR. COWLES: Those are chemical changes, are they not? Are not changes in concentration truly of the nature of chemical changes? Independent of their occurrence in a cell, would they not involve the absorption or giving up of heat energy?

MR. CARHART: The thermo-electromotive force between the electrolyte and the metal increases as the concentration increases. The change in concentration has, as a result, the change in the electromotive force.

MR. COWLES: The cell also gives up or absorbs electric energy in virtue of changes in concentration. Do not such changes call for an expenditure or absorption of energy to effect them?

MR. CARHART: I don't know. That is another question altogether. It is not what we are talking about. This is self-limiting. It cannot convert heat energy into electric energy except temporarily or through a small range, unless the cell is reversed and put through the series of changes represented by the Carnot cycle. In that case it would not be self-limiting, and therefore the production of current in that way is not contrary to the laws of ther-

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mo-dynamics, because we see we can carry it through a complete Carnot cycle of changes; and further, experimentally, we do not find the electromotive force between the two solutions equal to the difference of electromotive forces between the electrolytes and the two metals.

MR. COWLES: You have your solutions so dilute that there would naturally be no change of heat energy with the diffusion of the two liquids. Is that the case?

MR. CARHART: In case there is energy derived from the solution, that gives rise to a portion of the whole electromotive force which is totally independent of this other. In so far as the cell takes heat energy and converts it into the energy of the electric current, the electromotive force that does that is thermal in origin, and not chemical.

MR. COWLES: The heat absorbed or given off in chemical action varies with temperature. The capacity of atoms for heat, though theoretically equal, are not absolutely equal. Hence the specific heat of products that may be dissociated may be different from the same product when in chemical union. As you vary temperature, this difference undoubtedly leads to differences in heats of combination, and therefore by Thompson's rule differences in electromotive force. In other words, as we deal with heats of combination and voltages of disruption or formation, of chemical compounds, they are, in a measure, a function of temperature. It seems to me that such variations in the heats of chemical combinations would, under the first case just mentioned by you, lead to the very Carnot cycle that you have found. You are not dealing here with a concentration cell, and operating it without a change of temperature at all, as you have described in your former paper. You secured a flow of current with your concentration cell, which you attributed to a thermal cause. It seems to me that there must have been some source of energy other than the environment, to have caused that flow of current. That sort of energy must have come from the diffusion of the two solutions of unequal dilution into each other. Now the question I wish to put was, in cases of dilution so great that there is naturally no heat of solution evolved or absorbed during diffusion, and therefore no source of chemical energy, do we still get a conversion of current around the cycle?

MR. CARHART: Yes.

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MR. COWLES: Then it would seem as though your points were well taken.

MR. CARHART: Let me add just one word with reference to this electromotive force. One part has to do with the conversion of heat energy into the energy of an electric current; the other, due to chemical energy, is an electromotive force that comes from the internal energy of the cell.

MR. COWLES: That would be true.

MR. CARHART: Any such reasoning as that of Mr. Cowles would entirely do away with the second term in the Helmholtz equation; so, unless you wish to prove that the Helmholtz equation is incorrect, you will have to admit that the electromotive force of this concentration cell is thermal.

MR. REED: I would ask whether you do not mean, when you speak of the sum of the thermo-electromotive forces at the junctions being zero, the sum of the thermo-electromotive forces in the circuit, which includes not only those at the junctions, but also those in the conductors between the junctions, that is, the Thompson effect? The thermo-electromotive forces at the junction is only the sum of the Peltier effects, and the total thermo-electromotive force is the sum of the Thompson and the Peltier effects.

MR. CARHART: If there are no differences of temperature at the several junctions, the Thompson effect disappears. That applies, if I remember, only to cases where one part of the circuit has a higher temperature than the others.

MR. REED: As I understand these two effects, they are effects which convert one form of energy into another. There can be no such conversion either at the junctions or between the junctions unless there is a current flowing. If there is a current flowing, that of itself will in all cases cause both the Thompson and the Peltier effect. That then would necessitate some transformation of energy by the Thompson effect in a conductor between the junctions, so that the thermo-electromotive force is always the sum of those two.

MR. CARHART: But that statement is true if there were differences of temperature; if there were no differences of temperature then I do not understand that there are any electromotive forces except those at the junctions.

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MR. REED: There could not be any Peltier effect at the junctions except when the current is flowing. In that case there would necessarily be a difference of temperature, because the flowing of current would produce a difference in the temperature at the two junctions. One of them would necessarily absorb heat and the other would evolve it. There could, therefore, be no Peltier effect without a difference of temperature or without the Thompson effect, though there may be a Thompson effect in a circuit in which there is no Peltier effect.

MR. CARHART: If there is no electromotive force around the circuit, there is no current flowing.

MR. REED: Then there is no thermo-electric effect (laughter). As I understand the thermo-electric effect, it is the transformation of energy, and it could not occur unless a current is flowing.

MR. TOWNSEND: I would inquire with regard to a very minor point in Prof. Carhart's paper—whether there is any reason to believe that the electromotive force between carbon and carbon vapor is at all of such order of magnitude as to account for the difference in temperature between the positive and negative carbons?

MR. CARHART: One can hardly say. It is difficult to express it in that form. What Mr. Duddell did find was a thermo-electromotive force, as I remember, between two carbons, one of which was heated hotter than the other, artificially, not by electricity. The difference of temperature that will be established between the two carbons will depend upon the value of this thermo-electromotive force and upon the current flowing. Heat is absorbed at the negative and is generated at the positive. Mr. Duddell also found the value of this back electromotive force, but it varied with conditions; at all events, qualitatively the phenomenon is such as to tend to explain the well-known fact of the higher temperature of the positive electrode, and it is very interesting from that point of view.

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A paper read at the Third General Meeting of the American Electrochemical Society, New York City, April 16, 1903, President Richards in the Chair.

THE PROTECTIVE ACTION OF ZINC CHLORIDE ON METALLIC IRON.

By C. J. Reed.

It is now generally recognized that the rusting or oxidation of metallic iron in the presence of water and saline solutions is an electrochemical process, the water or saline solution being the electrolyte and the metallic iron the anode. Small particles of graphitic carbon and other impurities or alloys serve as cathode to form local voltaic circuits. This theory has recently received strong confirmation in the investigations of Dr. Carl Hambuechen, published in the Bulletin of the University of Wisconsin, July, 1900.

According to the theory of electrolytic dissociation, a saline solution consists of a mixture of free positive and negative ions with water and undissociated molecules of the salt. It is the supposed action of the chlorine ions in the case of the metallic chlorides, and in other cases the action of other negative ions, which causes oxidation.

According to this theory a solution of zinc chloride must contain an abundance of Cl-ions, which should be capable of attacking iron in exactly the same manner as the Cl-ions in a solution of sodium chloride, since the zinc chloride solution is an electrolyte and a very good electrolytic conductor.

About three years ago I noticed that pieces of iron which were accidentally left in contact with a strong solution of zinc chloride (sp. gr. about 1.30) appeared to be unacted upon after a considerable length of time. The particular solution used had been boiled for several days in contact with metallic zinc. In order to examine this peculiar phenomenon more carefully, a test-tube was filled with the solution to a depth of about 3 inches, into which were dropped some bright steel wire nails. The tube was set aside without being closed, and allowed to stand for about two years. During this period a layer of basic zinc chloride precipitated out in a

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white opaque stratum about a quarter of an inch thick at the top of the solution, but the nails in the bottom of the tube retained their original brightness and there were no traces of iron in the solution. The nails were then removed, washed and carefully examined. There was found to be not the slightest corrosion, the appearance of the nails being the same as when they were first dropped into the solution. The exact composition of this solution was not determined.

In a later experiment a number of test-tubes containing zinc chloride previously boiled in contact with metallic zinc and varying in sp. gr. from 1.10 to 1.35 were tested in the same manner, being allowed to stand in the open air for four weeks, each tube containing a number of small wire nails. A similar experiment was also made with solutions of zinc chloride (varying in strength through the same range), which had not been boiled in contact with metallic zinc.

In all cases it was found that no oxide of iron was produced on the nails. The zinc chloride solutions which had not been boiled with metallic zinc, caused, during the first few days, a slow evolution of hydrogen from the surface of the iron, showing that the iron was dissolving to a slight extent in the solution. This solvent action ceased after a time, leaving the surface of the nails unoxidized. The strong solutions which had been previously boiled in contact with zinc, appeared to have no solvent action upon the iron, the nails in these cases also retaining their original luster.

In the course of time (the exact time was not noted) the solutions which had not been boiled in contact with the zinc and which had shown signs of solvent action, began to deposit ferric oxide. The weaker solutions which had been boiled in contact with zinc also at the end of four weeks showed a very slight deposition of ferric oxide, the quantity of oxide being greatest in the weakest solutions. But in no case was the original brilliancy of the metal affected; that is, the metal had not rusted at any point. This shows that in all cases in which ferric oxide was formed, the metal was first dissolved into solution (probably as a ferrous salt), and afterwards precipitated as ferric oxide by atmospheric oxidation. But in the strong solutions which had been boiled with metallic zinc there was not the slightest action of any kind upon the iron.

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I do not know that these facts are of any practical value or whether they have been previously observed. But, I am not aware of their having been published before, and thought this peculiar action of sufficient bearing on the theory of electrolytic dissociation to merit it being brought to your attention. The advocates of electrolytic dissociation who are present will undoubtedly be able to give us an explanation and show why the chlorine ions in a solution of sodium chloride rapidly oxidize iron, while those in a solution of zinc chloride protect the iron from oxidation as perfectly as it would be protected in oil or dry air.

All of the solutions mentioned above were decidedly acid in their behavior towards litmus paper, turning it a bright red.

DISCUSSION.

MR. A. H. EDDY: Mr. Chairman, I wish to ask Mr. Reed what was the effect of the solution after the nails were exposed to air; after being taken out of the solution, did they then seem to have any further protection?

MR. C. J. REED: I did not make any test of that. The nails were carefully washed and oiled in order to prevent any subsequent action, because I wanted to show them as samples.

DR. LEO BAEKELAND: In regard to the facts which Mr. Reed just gave to us, I would like to call attention to the influence carbonic acid gas has on all those phenomena. I think those experiments would have been more interesting if they had been conducted by excluding air from the solution by boiling or by creating a vacuum, and afterward saturating the solution with chemically pure carbon dioxide.

MR. REED: I would say that the solution which I used, and in which this iron was preserved for two years was decidedly acid to litmus paper. It turned blue litmus paper red, showing the presence, according to the theory of dissociation, of hydrogen ions. In regard to the action of carbon doxide, Dr. W. R. Whitney, in the last number of the *Journal of the American Chemical Society*, describes some experiments, showing conclusively the very decided action of carbon dioxide on iron. I think he boiled some iron nails

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in water from which the air had all been expelled, and there was no deposition of oxide whatever, but apparently a solution of the iron in the water. As soon as air was admitted to the flask there was an immediate precipitation of ferric hydrate.

DR. N. S. KEITH: Mr. Reed, did you dissolve some sodium in your solution of chloride, or did you boil some soda in it so as to give a like physical condition, and observe the result? It seems to me that the zinc choride may have become supersaturated, though you say it gave an acid reaction. I do not think it is a fair comparison unless some sodium or soda was dissolved in the sodium chloride solution.

MR. REED: If you boil sodium in the water, or put it in without boiling, you will get a solution which is distinctly alkaline, and which, according to the theory of electrolytic dissociation, does not contain hydrogen ions—free hydrogen ions—but contains hydroxyl ions, which have the opposite effect. An experiment of that kind would therefore be of an entirely different nature; it would not be comparable to this.

DR. KEITH: I once had my little finger blown off by attempting to boil sodium in water.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

INSULATING MATERIALS, A FIELD FOR THE CHEMIST.

By Max von Recklinghausen.

The great hopes we had at the beginning of the last decade as to the future of the electrochemical industry in its purest form, that is, as technical *electrolysis,* were not all realized. The main advance during this time in the—I may say—electrical manufacture of chemical and similar products has been due not to the use of the current as electrolyzer but to the application of the electric current as a source of heat for chemical and physical reactions which heretofore, if known at all, were only feasible on a laboratory scale.

The manufacturing chemist is the one who has gained enormously during this time, because the electrical engineer has put at his disposal heat sources of an undreamed-of magnitude.

The advance in electrical engineering has enabled the technical chemist to economically use high temperature reactions for making products and compounds which until then were scarcely obtainable in the laboratory.

The electrochemist is therefore under the greatest obligations to the electrical industry. It is only fair that he should show his gratitude by helping the electrical engineer out of his troubles in a field where his chemical research is of vital importance. I mean the field of the *electrical insulating materials.*

Up to now, the electrical engineer, in most cases, has been left to himself to find the best insulating material for his particular purpose. All he could do, was to pick out the most promising ones among those offered to him by the trade. But he is far from having the ideal materials for the different types of insulation, especially for high tension work, which is greatly handicapped by the lack of suitable insulating materials.

This is therefore the time when the chemist should step in and use his knowledge and ability for producing for the electrical engi-

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neer insulating materials that are better and more satisfactory than those obtainable to-day.

While there are doubtless many chemists, especially among the makers of varnishes and oils, etc., who are on the outlook in this important field of electrical insulating materials, one must say, that among chemists generally there is but little interest in these matters and generally small appreciation of the enormous value that chemical work in this field would have for the advance of the electrical industry.

One can safely say that one of the main reasons why the electrical engineer gets little help in this field from the chemist, lies in the fact that the chemist does not appreciate the different wants of the electrical engineer. It happens over and again, that chemists offer materials for insulation, which may have *one* good property, may, for instance, have enormous resistance to the passage of current, but be so highly inflammable or with so low a melting-point as to be utterly useless for the purpose intended.

In the following, I shall try to give a general idea of the desirable and the undesirable qualities of the prominent insulating materials used nowadays, and shall furthermore try to point out where chemical research would be particularly important.

To start with, we have to classify the properties under which the different insulating materials have to be considered.

I.—*Electrical Properties*:

A. Insulation resistance or conductivity, expressed in ohms per cubic centimeter.

B. Disruptive or dielectric strength, measured by the high potential voltage necessary to puncture the material.

C. Dielectric constant or specific inductive capacity measured by the capacity in microfarads of a condenser having the particular material as dielectric separating the metal plates. (This property is less important than the ones mentioned under *A* and *B*.)

II.—*Mechanical Properties*:

A. Strength and workability. (For solids.)

B. Flexibility and workability. (For semi-solids.)

C. Viscosity. (For liquids.)

III.—*Chemical Properties*:

A. Combustibility.

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B. Property of resisting influence of moisture (hygroscopic quality), air, oil, acids, etc.

The factors which may considerably influence the properties of the insulating materials during use are the following:

I—*Rise of Temperature* (going as far as melting or charring organic materials) due to:

A. Current passing in virtue of the insulation resistance, with not enough chance to radiate the heat generated.

B. Heat conducted into the insulating material from outside sources, such as the metallic conductor.

C. Dielectric hysteresis, due to very frequent application and withdrawal of high electrical stress, such as high voltage alternating current, with not enough chance to radiate the heat generated.

II.—*Mechanical Stress*, resulting in change of shape or breaking.

III.—*Chemical Action*, of, for instance, water, oil, ozone, nitrous fumes (which may be generated by brush discharges near-by), gases and fumes developed by factory processes in the neighborhood of the electrical apparatus.

Desirable qualities are mainly good insulation resistance, high disruptive strength, fair mechanical properties, especially workability.

Undesirable qualities are mainly combustibility and changes in the electrical and mechanical properties with rise of temperature or with age, and, of course, *high-price.*

To chemically classify the insulating materials, it is practical to consider them under the headings of:

I.—Organic materials, liquid and solid.

II.—Mixtures of organic and inorganic materials.

III.—Inorganic materials.

I. *A.—Liquid Organic Materials*:

This chapter comprises the materials used mainly for transformer insulating and cooling, for condensers and more recently for circuit breakers.

Such liquid insulators are the different *oils* and other liquid organic compounds.

Most properties of the oils as used now are desirable. The

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worst feature inherent to them is their *combustibility*. Flash test and viscosity test (and influence of long-continued use on the same) give a good idea of the usefulness of an oil for the purposes mentioned above.

In case of circuit breakers, as well as of transformers, where accidental high potential may have broken through the oil, the broken-down oil insulation should soon be repaired and the oil should come back to its original insulating power. At the same time it would be well that such oil does not develop too much low-flash products which bring with them the danger of fire.

In circuit-breaker work, some oils will break the arc off very sharply with corresponding back effect on inductance in the line, others will be slower in their action and may thus be more useful for such purposes.

Naturally one has to study the effect of the oils on the different materials they come in contact with. Fatty acids seem to be undesirable in such respects, because they are apt to react with copper.

To do away with the worst feature of oils, their combustibility, one has proposed to use *halogen carbon* compounds, instead of hydrocarbon compounds. It is distinctly worth investigating whether the products resulting from such liquids when the discharge goes through would be of too bad an effect on the apparatus. For instance, tetrachloride of carbon would probably break up into carbon and free chlorine and the latter would very likely injure the metal.

I. *B.—Organic Compounds Used in a Solid or More or Less Plastic State.*

Typical representatives of this long line are the different varnishes, lacquers, drying oils, rubber, compounds made from blood, glue, all the different cellulose materials, such as used for textile fabrics, wood and mixtures of the different materials belonging to this group. It will be rather hard work to make material advance in this field by further research, as the makers of these materials are continually on the outlook for improvements and continually making them.

I mainly want to point out some of the disadvantages of the materials used nowadays. Many of them lose their mechanical strength and their insulating power and dielectric strength by age

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and by short or long duration of high temperature and high electric stress. All of them are more or less inflammable. Here is probably the point where a thorough chemical research could find a field. The pure cellulose compounds are probably very good in every regard, especially because they seem to be less affected by heat and less inflammable than the other materials of this group, but up to now, they are fairly difficult to get into the desired dense mechanical shape. Nitrocellulose and other celluloid compounds are ideal in this way, but of course are out of question on account of their combustibility. New artificial masses such as viscose, cellulose made out of cellulose solution in acids, metal salts, etc., and similar products may very well be worth experimenting on because they are free from nitro-groups and, therefore, are probably little affected by heat. Also glue and gelatine compounds made insoluble by different methods ought to be examined for their usefulness as insulators, and, if necessary, chemically modified so as to compete successfully in properties and price with materials used now.

One point is important for dynamo and especially transformer insulation, *i. e.*, that the oil used should not have a dissolving or other effect on the insulating material. Furthermore, the insulation should not be affected by moisture which often in large amounts covers cold apparatus brought into warm rooms.

Complaints are heard of the attack of some varnishes on particularly thin wires. For such purposes it may be good to prevent direct touch of the varnish and the metal by an intermediate coating.

Attempts are being made lately to produce asphalt compounds which seem to have many excellent properties; still it will be fairly hard soon to find materials electrically and mechanically desirable but unaffected by oil and water.

I scarcely need mention the old problem of finding a replacement of the expensive gutta-percha.

II.—*Mixtures of Organic and Inorganic Materials.*

Typical representatives of this group are mainly materials made of asbestos or mica with varnish, rubber or paper, or similar materials out of the group mentioned before.

The asbestos compounds, as a rule, lack flexibility and high

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insulating power, also mechanical strength; the mica papers lack great flexibility and homogeneity

III.—*Inorganic Materials.*

The representative materials of this group are slate, marble, asbestos, porcelain and glass. They are, of course, practically unaffected by heat, but lack entirely flexibility and are furthermore fairly expensive to form into the desired shapes. Better in the latter regard, but not as good insulators, are cement-like mixtures made out of water glass and asbestos, or similar minerals. Progress in this field may be expected in the line of the cements, which can be cast, although up to now they seem to be too hygroscopic.

That even the mineral insulators become conductors at high temperatures has been found out by people working on the Nernst lamp, where after finding a good conductor at high temperature for the glower part one had great trouble to find a good insulator for high temperatures for the heater part.

The main objection to marble for switchboard work is the great expense. Anything to replace marble would be of greatest importance. It should, of course, not be hygroscopic at all.

Sometime ago this was found to be important for high-tension line insulators. The makers were careful to make the insulators absolutely non-hygroscopic by choosing glass free from alkali. Still the beneficial effect of this is to a certain extent overrated, as the heat developed by the leakage current is enough to remove the water which may condense on the insulator.

A tremendous step forward for the electrical engineer would be an insulating material of the flexibility of asbestos and the ideally high insulating and dielectric strength of mica.

I have tried to give you, in the limited space at my disposal, an idea of the work which could be done in this line, and I hope you agree with me when I say that it is a field of very great importance and it would further the electrical industry and therefore all those industries depending on it. I should be very glad, indeed, if I should succeed in inducing my fellow chemists to consider more than heretofore the large and important field of electric insulating materials.

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AN HISTORICAL REVIEW OF THE STORAGE BATTERY.

By H. B. Coho.

The vast strides that have been made in the use of the storage battery and the many advantages claimed by the various patentees as to the durability and efficiency of their cells naturally leads to the question as to what improvement, if any, is to be found in the storage cells now employed over those of former days.

There has been a doubt in the minds of many engineers as to the desirability of a secondary receiver, but up to within a very few years it was indeed a very courageous engineer who dared to recommend to his clients the use of an accumulator.

The field of research along the lines of storage battery development is of particular interest to the electrochemist, as both the chemical and electrical sciences enter largely into his calculations, and there is probably no field wherein the reward would be greater could certain elements or combinations of elements be found that would be capable of doubling the output of the present lead cell without increasing the weight or bulk of the battery as a whole.

The consulting engineer is called upon more frequently perhaps to pass upon new batteries than upon almost any other subject, and as it is important that any meritorious discovery be carefully investigated, great care has to be given to this subject.

As a matter of fact, one of the easiest propositions in the storage battery field is to build a cell of light weight and to get a great output for a short time, but when that same battery is called upon to give its output under the varying conditions met in an automobile, for instance, the result is generally disastrous to the light lead cell.

The amount of money which has been lost in the endeavor to force upon the market secondary batteries having little or no intrinsic value, to say nothing of the heartaches to honest inventors from unfulfilled dreams, makes the history of the storage battery's

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development almost tragic, and now that the Brush patent has expired there will probably be a new growth to be cut down by the ruthless test of durability, and this, therefore, seems to be a fitting time to review briefly what has been done and to give short descriptions of some of the more important experiments covering the discovery of secondary currents, as well as to describe a few of the more important types of cell.

The first attempt in the storage of electricity was that of Musschenbroek in 1745. He only succeeded in storing it in a bottle for ten, twenty, thirty or more seconds, and his discovery was of no practical value. It, however, led to his discovery of the principle upon which his invention of the Leyden jar is based.

In 1783 Volta invented his condenser, based upon the same principle, while in 1800 he invented the "Crown of Cups" voltaic pile, a battery consisting of two different metals and a liquid.

Humboldt in 1796 observed the phenomenon of what later became known as "polarization." He noticed the action of a plate of silver brought into contact with a moistened plate of zinc, and the action between other metals when in the presence of water. Humboldt directed attention to the decomposition of water into its constituent elements, and he created the phrase "decomposition of water by galvanic action."

The year 1801 saw the inception of what might be termed the scientific era in the history of the storage battery, which terminated with the advent of Plante's first practical cell. It was in this year that Gautherot, a French scientist, discovered that platinum or silver electrodes which had been used in the decomposition of a saline solution by the current of a voltaic cell, after being disconnected from the battery itself, were capable of giving an electric current lasting but a few moments. Carlisle and Nicholson experimenting with the electrolysis of water are said to have "unwittingly constructed an apparatus vaguely resembling an accumulator."

Erman in 1801 found that the electrode connected with the positive pole of a voltaic battery, after being disconnected from the cell, will return a positive current, and he is said to have discovered the principle of polarization.

In 1801 Ritter observed the same facts. He succeeded in decomposing water by means of the polarized electrodes and demon-

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strated the inversion of the currents. In 1802 he made the first secondary battery. This battery consisted of a pile composed of disks made of copper plates, separated by a liquid. The liquid became charged when the current of a voltaic battery was passed through it, and produced all the characteristics of a primary battery.

Gautherot's discovery was confirmed by Ritter in 1803, except that Ritter used gold wire and made a secondary battery by superposing a series of pieces of gold between circular pieces of cloth which had been moistened with a saline solution. Ritter is said to have always used a saline solution instead of acidulated water.

In his experiments he found that copper was not the best kind of metal for secondary batteries, and he tried bismuth, brass, gold, iron, lead, platinum, silver, tin and zinc. He had the most success with carburet of iron and peroxide of manganese, and he obtained no results with lead, tin or zinc. It is interesting to note here his reason for not employing lead in his secondary batteries. In the saline solution which he always used, lead chloride formed on the negative electrode, and this being but very slightly soluble, as well as a very poor conductor, the primary current itself was not strong as compared to that produced in acidulated water.

It was thought at the time that the secondary currents were due to the recombination of the acids and bases yielded during the decomposition of the salts by the current of a voltaic battery. In 1826 De la Rive noticed similar secondary currents produced by a voltameter composed of platinum plates immersed in acidulated water, or even in distilled water. The absence of salts to be decomposed and the fact that the metal was not oxidized led to the belief that the secondary currents were produced by a physical rather than a chemical action, and the electrodes were said to be "polarized."

Becquerel, Marianini and Volta have shown that Ritter's secondary currents had a chemical origin. Becquerel proved that the current produced by a secondary battery was due to the reciprocal action of an acid and its base. He immersed one of the platinum plates in an acid and the other in a basic solution, and these were united by a moist conducting material. The plate immersed in the acid solution became the positive pole, while the plate in the basic solution became the negative pole. This led to

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the detection of the direction of the current of the secondary battery, and this direction was such that the plate in connection with the positive pole of the primary cell was actually the positive pole of the secondary battery.

Nobili's experiment is next recorded in 1826. He is said to have deposited peroxide of lead on lead plates by means of a primary current.

Schoenbein in 1837 showed that lead plates prepared with peroxide of lead were capable of giving a current similar to that of a primary battery.

Grove in 1842 made his famous gas battery with platinum strips, which, having previously been used for the decomposition of acidulated water by the current, would, when the battery was disconnected, cause the recombination of the hydrogen and oxygen, thus producing an inverse current.

Faraday observed in the electrolysis of a solution of lead acetate that peroxide of lead was formed at the positive electrode, while metallic lead was produced at the negative pole. He found that the peroxide was a very good conductor and observed its ready ability to yield its oxygen.

Grove discovered in 1843 that plates covered with the oxides of metals gave better results than metal plates. Siemens used carbon plates in the same year, and Wheatstone made a secondary battery of platinum plates covered with the peroxide of lead and potassium amalgam, but they both found that the peroxide of lead appeared to give the most satisfactory results for these purposes.

In 1853 Siemens used carbon plates covered with lead oxide, which was converted into peroxide by the current, but like its predecessors it belonged to the scientific era.

Plante in 1856 began his investigations with secondary batteries and in 1859 he discovered that lead was the best metal for them. In March, 1860, he constructed the first practical accumulator, which was based upon the property of lead as a powerful depolarizer, a fact that Faraday, Wheatstone, De la Rue, Niaudet, Sinsteden, and others observed before him, yet it remained for Plante to perceive the possibility of giving the secondary battery the power, capacity, permanence, and efficiency necessary to a practical accumulator, and his discovery brought with it the dawn of the practical era in the history of the storage battery.

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Plante's cell consisted of two coiled sheets of lead separated from each other by heavy cloth. These plates were immersed in dilute sulphuric acid. Upon sending a current through the liquid from one plate to the other some twenty or thirty times and frequently reversing the same, the positive plate became coated with lead peroxide, while the negative plate became "spongy," a process of "forming" which rendered the plates active.

In 1861 Kirchoff made batteries consisting of alternate plates of spongy lead and peroxide of lead.

Percival in 1866 experimented with metal plates covered with crushed coke and powdered lead in a solution of dilute sulphuric acid. It was for this battery that the first United States patent was granted for a storage battery. In 1869 he used a positive plate of amalgamated zinc and a negative electrode of lead.

It is recorded that Faure in 1872 attempted to obtain a secondary battery, and he is said to have improved his battery by perforating the plates and alloying the lead of the supports with antimony.

D'Arsonval in 1879 tried carbon plates covered with an oxide of lead and manganese, and with plates of zinc in a solution of zinc sulphate.

Plante's cell was practical in that it was powerful and utilizable, but the time required to form the plates was a factor that undoubtedly retarded its commercial adoption and one that received the attention of many eminent scientific men. Plante himself continued his researches until 1879. In this same year Metzger devised a means of applying the active material by a mechanical process which dispensed with Plante's slow-forming process.

In 1878 Faure conceived the idea of his secondary battery and discovered spongy electrolytic lead obtained from insoluble oxides, its value as a positive material and its practical manufacture. He constructed a battery with its elements made entirely of lead sulphate.

Reynier in 1880 invented his regenerating alkaline battery, but soon abandoned it and took up the Faure accumulator, with the inventor of which Reynier worked for many years.

In 1881 Faure took out a patent covering a method of getting the reducible plate by means of preparing the active material from oxides or salts mechanically applied to the surface of the plates,

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thus doing away with the great number of reversals required in the Plante cell. This saved power and reduced the time element, of which so much of either was required to form the plates of the Plante cell. A difficulty experienced in making the Faure or "pasted" cells was to keep the coatings on the plates, and heavy cloth was employed to facilitate this.

Swan and Sellon made the next improvement in the Faure cell. They introduced the substance which formed the coatings into the interstices in the lead.

After Faure obtained his patent in 1881, inventors in the United States, England, Germany, France and Italy and in other countries patented so-called improvements on the Plante and Faure types of cell. Confining research for the data for this paper entirely to the litigation in this country, owing to limited time and space, the difficulty in deciding the matter of the patent rights of the numerous claimants can be readily conceived when it is stated that in the patent office one decision alone is said to have been reversed twelve times before the case was finally decided.

In 1882 Gladstone and Tribe were the first to declare that sulphuric acid had a direct action upon the electrodes, and they also made the statement that "the principal, if not the only, function of the hydrogen of the water is that of reducing the lead compounds."

In 1885 a patent was issued to Brush by the United States Courts, after long litigation, for the mechanical application of oxides of lead to a supporting grid of conducting material, as it was decided that Brush's invention antedated Faure's application for patent. Brush received other decisions in his favor in this country, while a compromise was effected before decision was rendered in the Brush-Julien litigation.

Since Plante's time Reynier's lead-zinc cell, Sutton's copper-lead cell and the Thomson-Houston copper-zinc cell have been devised, while another type of cell that appeared after Reynier's cell was the alkaline-zincate secondary battery, which had one zinc electrode and an alkaline electrolyte. The Desmazure, Edison-Lalande, Lalande-Chaperon and the Waddell-Entz storage batteries are of this latter class.

Nickel was used in accumulators by Dun in 1885, and porous

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nickel electrodes were used by Desmazure in 1887. Michalowski in 1889 discovered a new method of making nickel electrodes.

Pollak in 1896 experimented with iron compounds, while Krieger invented a cell using nickel.

In 1898 Jungner made cells, using copper and cadmium-silver electrodes.

The chloride battery consisted of plates cast of a fused mixture of chloride of lead which had a rigid metallic rim cast about them. When immersed in a solution of chloride of zinc or a similar substance in connection with a piece of metallic zinc, the chlorine in the zinc chloride and in the lead chloride combines with the zinc plate and forms zinc chloride. Thus prepared the plates are ready for use in the same way that Plante plates are when "formed."

In his first cells Edison used cadmium and copper in an alkaline electrolyte.

A patent was issued to Edison on February 4, 1902, for a storage battery consisting of sheet iron or steel grids, nickel-plated, to prevent the electrolyte of potassium hydrate from acting on the same. The grids have a series of openings into each of which fits a pocket made of thin crucible steel with perforations having internal burrs. These pockets contain briquettes of finely divided cadmium, which is used as the oxidizable element and an oxide of nickel or cobalt which is used as the depolarizer. The plates are placed alternately, and between them are placed rubber partitions.

In the foregoing historical sketch it will be seen that the main points intended to be brought out are the various metals, compounds and electrolytes that were used in experiments by the leading physicists in the past, and it is hoped that this will prove of service to prospective inventors.

The history of storage battery installations has been covered by a number of writers, and the following are only intended to give a few of the early uses to which the storage battery was put in so far as it was possible to get definite information on the subject at this time.

In 1882 one of the first storage battery installations was made on a car belonging to the Pennsylvania Railroad Company for the purpose of train-lighting, but this experiment did not result satisfactorily. The cells for this purpose were imported from France.

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One of the first isolated plant installations was made with electric power storage cells imported from England, in Baltimore in 1883. The battery was used for incandescent lighting in several stores in the vicinity where it was installed.

The first storage battery installation in a central station is supposed to have been in Phillipsburg, Pa., in 1885.

In 1886 an electric boat "Volta" made a trip in the English Channel, and the trials of the submarine boat "Nautilus" took place, both boats being equipped with Elwell-Parker cells.

Applications of storage batteries became quite general about this time, and while a good many of the earlier installations were failures, yet the demand caused the manufacturers to improve their cells to meet conditions.

In his specification for an invention, Faure, in 1887, claimed an improvement "in the application of secondary batteries or accumulators preferably carried by a vehicle or upon one or a train of vehicles to supply electrical energy to one or more electro-magnetic motors, also carried by or upon said vehicle, or one or more of a train of vehicles, combined with means for varying the amount of energy supplied by the battery." The Commissioner of Patents decided that the combination was not new and therefore not patentable, and attributed the commercial success of the alleged invention to the Faure battery alone, and not to the combination. The Supreme Court of the District of Columbia affirmed this decision, the case having been appealed.

The first important installation of modern storage batteries of German manufacture was made by the Edison Electric Illuminating Company, of Boston, in 1894, and in 1896 they installed their first American cell.

As is well known, while comparatively little improvement has been made in the manufacture of the secondary battery, yet the necessity for its use from engineering and commercial standpoints is plainly evinced by the many purposes for which it has proved itself practical and for which it is being constantly demanded.

As indicative of the amount of business done in storage batteries, the Electric Storage Battery Company, of Philadelphia, has installed up to date about 85 central station plants having a capacity of 120,000-kilowatt-hours; 225 railway batteries having

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a capacity of 160,000-kilowatt-hours; and 500 isolated plant batteries having a capacity of 30,000-kilowatt-hours.

It might be well to mention here that theoretically there is no difference between a secondary battery and a primary battery, as in both the chemical energy becomes transformed into electrical energy. If peroxide of lead prepared by electrolysis is placed around a cylinder of lead and put into acidulated water with another cylinder which has spongy lead similarly prepared placed about it, the cell would ordinarily be called a primary cell, while if a reversed current is passed through a Daniell cell, the cell would become a storage battery. Other well-known primary cells, if treated in the proper way, could be made secondary batteries. It is entirely a matter of a reverse current, and it is in this that the lead peroxide battery has up to the present time demonstrated its practicability over other cells.

One of the most recent inventions is in a patent granted to Edison on March 3, 1903, covering a modification in his alkaline storage battery. The electrode is composed of oxide of cobalt mixed with metallic mercury or with metallic mercury and copper or silver, by which a great proportion of the cobalt oxide is kept in electrical contact with the electrode. Mercury, copper or silver are added by preference to the oxide of cobalt for the purpose of maintaining contact between the active materials, but any insoluble conducting material, preferably in flake form, such as flake graphite, can be used for this purpose.

DISCUSSION.

DR. H. S. CARHART: Mr. Chairman, I should like to add a small item to the historical part of this subject. I happened to be present in 1881 at the Paris Exposition of Electricity as one of the International Jurors for the United States, and during that time I became acquainted with M. Planté and was invited to go to his laboratory to see his storage cells. I went in company, I remember, with Prof. Barker. During that visit, I remember with very great distinctness, Planté told us that he had some time previously tried the application of active material to his plates and found that he could not get as good results as he got with the formed plates. He

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did not publish this; he did not apply for a patent; I think he never obtained any patent; and in the public mind has not had credit for the application of active material to the plates. That is the point that I wish to add to this paper.

DR. N. S. KEITH: I desire to add a little to the historical interest in this matter by stating that I was one of the early litigants with Brush before the Patent Office. I received a patent, after extensive efforts in that line, for a storage battery made by depositing peroxide of lead upon the anode in a now well-known way, and using those plates as the positive and negative by the reduction of the lead upon the one plate to metallic lead—the oxide to metallic lead upon the one plate—and retaining the peroxide deposited by electrolysis upon the other. It was shown by the testimony that I made my storage battery in that way in the year 1877 or 1878 here in New York City.

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THE USE OF PYROXYLINE IN ELECTRIC STORAGE BATTERIES.

By Elmer A. Sperry.

Mr. Coho just spoke of the Boston Edison Company as being the first in this country to put in a large station battery and it is interesting to note, in connection with this installation, that those old batteries imported at that time from Germany are still in service. I happened to be present some time ago when one of those batteries had been taken down, washed, reburned and put in service; and, as indicating what we can now depend upon from storage batteries, let me say that they found it gave, as a matter of fact, 118 per cent. of its original claimed capacity. Of course, it has always worked over and above the claimed capacity. That was the Tudor battery of Germany, and is good evidence of the commercial possibilities of the storage battery.

I saw at Paris in the nineties some of the old batteries of Planté, and was struck then as I have been since, with reference to these earlier workers, by one fact that has a bearing on the question before us; that is, that they all used envelopes. We remember Planté's as a sheet of lead rolled upon itself, with flannel used as a separator and an envelope at the same time. In all Faure's earlier work he used felt; and our own C. F. Brush, in Cleveland, in his first conception of the application of active material, held it on with blotting-paper; and the records of the patent offices, both domestic and foreign, show the struggle ever since for a material that would stand up in a commercial way under severe conditions. It has been proved by one of the founders of this organization, who is here present, that if the peroxide on the positive plate can simply be securely held in mechanical contact with the lead plate, practically its full theoretical value can be obtained. I do not mean theoretical value strictly, but the full value that we ordinarily obtain, which is only a certain per cent. of its theoretical

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value. This work shows that if the peroxide can be held on, nine-tenths of the battle is won; for, as we know, the great difficulties encountered, especially in automobile and traction batteries, or in all portable batteries as a class, is the surface wash. The surface wash, with moving electrolyte, is a peculiar action. The electrolyte in immediate contact with the positive plate is constantly in motion, and especially so when the battery has approached its point of full charge, as we know the upwardly rushing bubbles then cause a very vigorous wash. This does not seriously affect the envelope, nor the negative element of a storage battery; the negative element it seems has proved abundantly able to take care of itself, but the positive is different. This element expands and contracts during every charge and discharge; and then it grows gradually, so that effective protection of it, the armoring, you might say, of its face, becomes really quite a problem; and, as I have before said, many have undertaken to accomplish this and with more or less success.

The first application of pyroxyline to storage batteries was at the hands—and very able hands I may say—of Desmond G. Fitzgerald. While at his laboratory in London, some years ago, I was struck with the varied forms in which Fitzgerald had been enabled to make this material. His plan, however, was to commingle it with the peroxide and use it as a cementing substance to make the peroxide more closely adherent to the electrode proper; and he was more or less successful in this; but the trouble was that when the cement was reduced down to a point where it did not interfere with the rapid discharge of the battery, it did not act very well as a cement and allowed the positive plate to easily disintegrate and surface-wash into the cell.

Another point with regard to the difficulties with the positive, especially in the hands of the non-expert, is its "boiling." When a battery is nearly charged, the current should be reduced to a low value, but in the hands of the non-expert the higher current is sometimes continued, resulting in "boiling" the battery; the positive plate flakes off and becomes soft, even though the positive material may be originally formed on the plate so hard that it resembles sandstone; the material will commence to loosen up and soften at the surface, probably somewhat through the action of

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the rising gases on the surface and the surface-wash that I have described; and it is the duty of the envelope or of some protecting armor to hold those materials and keep the peroxide up in place on the plate as long as possible.

I have spoken of the wide-spread appreciation of the function performed by the envelope. To be successful, the material should have toughness and flexibility, and a certain amount of elasticity to accommodate itself to the creeping or expansion and contraction of the positive. Of course, the material should be such as to be made very thin, with the maximum degree of porosity, because its effect on the internal resistance of the cell is very marked if it is allowed to become thick to any degree. The proper porosity is something that I have given quite a little attention to; and I find that the envelope has to be very porous, enough so, in fact, that the internal resistance is practically negligible, on a four-hour rate. I find another rather interesting feature: by proportioning the thickness or mesh of the pyroxyline fabric or fiber—we have used it in several forms—; or for instance, by putting on enough layers we can make the function of the internal resistance felt at the right time, namely, at the time of short-circuit, or at the time the battery tends to discharge much more rapidly than with any normal requirement, and in this way it can be used as a valuable safeguard, because only at those times it commences to be felt and holds the rate of supply of current from the cell within safe limits.

So far as the chemistry is concerned, the pyroxyline should have a molecular structure which is not broken down by the nascent oxygen evolved, which is not an easy matter. When we first commenced to use pyroxyline the best that we could do was to provide an envelope that would withstand about five discharges, when it would commence to disintegrate. The final form that this material has assumed is a fabric; and as you can see here, it is very porous; it looks like cloth, and, as originally made, it has long fiber. We find that when it has shrunk about 25 per cent. after nitration, it will have about the right degree of nitration for the certain amount of elasticity which we find necessary, combined with sufficient strength. The production of a pyroxyline fabric having the desirable characteristics is as follows: The fabric preferably having or being of long fiber, is first freed from all

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traces of soluble starchy matter and oleaginous matter. These points are important, because if there is a least trace of starchy or oleaginous matter in the material, upon nitration it goes into a paste and will not retain its original form; and that is true even where the hands of operatives are allowed to touch it. This we find is best accomplished by successive boilings in pure water and afterwards thoroughly drying. We have found that the best manner of drying is the sulphuric acid wash-bottle method, where the moisture is first taken from the air and then the air heated before allowing it to go over the material. Having been thus prepared, the fiber or fabric is subjected to the nitrating mixture. The present nitrating mixture consists of about 113 parts of nitric acid and about 150 parts of pure sulphuric acid (sp. gr. 1.84). The per cent. of nitric acid and sulphuric acid may be varied slightly with the season or the amount of humidity in the air, we find; but for good results it is better to adhere to practically a solution with these constituents.

The water and the starchy matter seem to be the worst enemies. If, for instance, in the nitration, any material is not entirely submerged and is allowed to absorb the least moisture from the atmosphere, any part of the material that comes above the surface is found to fall away on touching, showing the care that has to be exercised on these points. Then another point—to secure the elasticity—we find that the temperature must be below 75° F. As soon as the fiber is removed from the nitrating solution it is washed and neutralized, and made hygroscopic. As in the samples furnished, you can feel the moisture plainly. It can be rendered hygroscopic by adding a small quantity of nitro-benzole to the final washing. This is an important matter in the mechanical handling of the stuff in the factory and in shipping. We have now had about five years' experience with this material, during which time a number of thousand pounds has been made and used in its various forms. The data I have given is the final data that we have; that is, as good as we have up to the present time. We hope it is not final; although we have used so much of this, we never yet have had the first accident and have never had any accident reported from other places where the material has been used. Our practice is to wind the pyroxyline upon the plate tightly so

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that the elasticity may be utilized; the armor-like action will be apparent as the pyroxyline instead of the peroxide surface is exposed. We overwind our plates—under tension stack them up and then assemble; the lead strip acting as a connector is burned on by the oxy-hydrogen flame; this is used by a line of men at the benches. The pyroxyline, though often in the flame, never burns, and to show you this, I have asked the boy to bring some water. These plates are simply the slightest bit moist, because they stay on the benches sometimes a day and a night before they are burned together. Now this is just moist. (Touches a lighted match to the article.) You see it does not burn at all when it is damp.

As to the practical effects of the application of this material, we have found that we need quite considerably less grid factor for the plate, then the plate may be made simpler and still retain the active material in place. This envelope helps to do that and we get an increase of active material factor, a considerable increase of life and decreased amount of attention and washing. This is illustrated by the fact that we are enabled to make batteries, we find, with a very small mud space at the cell bottom. In traction batteries we find this need be only ⅜ to ⅝ inch for a two years' service with no short-circuits. This gives us a somewhat smaller jar for the same work. I have mentioned the fact that it can be employed to throttle the current flow on short-circuits, and on the whole we feel that we have produced a material having a combination of some new qualities, which I hope will have a wide scope of usefulness.

DISCUSSION.

DR. BAEKELAND: Mr. President, I would ask Mr. Sperry whether that cheese-cloth is nitrated, and woven afterwards, and whether he has any trouble in getting the starch out of the material.

MR. E. A. SPERRY: We had trouble at first; we don't have trouble now.

DR. BAEKELAND: In order to extract starch from that material have you tried the following method, which is a rather practical

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one: Boil simply with hot water, and afterwards let it cool down to about 70° centigrade and add an infusion of mallow?

MR. SPERRY: We have not tried the method named, but we will be very glad to see what it will do for us.

MR. HERING: I would like to ask Mr. Sperry how long he has had that in actual use in batteries—this final product.

MR. SPERRY: We have had a product that resembles this, but not as tenacious, for five years; and we have had one set of batteries on automobile work that have been in continuous service during the seasons for three years. It cannot be used in connection with the negative plate. The reducing action of hydrogen is quite well known on all materials of this nature—it is shown by the action of hydrogen on celluloid—it seems to gradually disintegrate; but where it is kept away from the negative it seems to be practically constant. Nascent oxygen has no effect—the electrolyte or electrolytic action has practically no effect upon it.

MR. C. J. REED: I obtained a piece of this material about a year or two ago and put it into sulphuric acid of the strength I was using in storage batteries, and left it for a couple of weeks and then found it had no strength whatever—it simply crumbled to pieces on touching it. I did not know whether that was a defective piece or what was the trouble.

MR. SPERRY: Are you sure, Mr. Reed, that it was not cheese-cloth?

MR. REED: It had the same inflammability—it ignited with a flash just like this sample.

MR. SPERRY: Piece that had been rejected probably.

MR. REED: I did not know but it might have been destroyed by some accidental exposure. Is there any danger of that?

MR. SPERRY: I cannot understand it acting in that way if it had ever been put on a plate.

MR. REED: No, it was just dipped in a jar of acid and was allowed to stand.

MR. SPERRY: If it was material that had been on a plate it ought to have been good stuff.

DR. W. H. WALKER: I think the degree of nitration of the cellu-

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lose has a very distinct effect upon the solubility, so that the piece Mr. Reed used may have been one that was very slightly nitrated.

MR. SPERRY: Possibly that answers the question.

MR. REED: I thought there must have been something defective in that particular piece. I did not wish to convey the impression that I had any doubts about any of the statements Mr. Sperry has made. I thought he might be able to explain what was the matter with the piece I had.

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A paper read at the Third General Meeting of the American Electrochemical Society at New York City, April 16, 1903, President Richards in the Chair.

CONCENTRATION CHANGES IN THE ELECTROLYSIS OF BRINE.

By W. H. Walker.

From the early days of 1851 when Charles Watt took out the first patent for the manufacture of caustic soda and chlorine by the electrolysis of brine, until the present day, the electrolytic method of preparing these two important chemicals has claimed the time and energy of many investigators. In its simplest form an apparatus capable of bringing about the reaction resulting in the formation and recovery of caustic soda and chlorine may be thought of as comprising a resistant receptacle or cell which carries two electrodes of opposite polarity, and is divided into two compartments by a permeable or semi-permeable membrane called the diaphragm. This is, however, the form which involves the most difficulties, both theoretical and practical; and while the processes using mercury cathodes or those employing molten salt as the electrolyte are the ones best suited to large installation, it is these so-called diaphragm processes that adapt themselves most easily to the conditions obtaining in small plants where the production of caustic and chlorine is secondary to other manufacturing processes. A consideration of the factors involved in controlling the commercial efficiency of such cells becomes therefore a matter of considerable technical importance.

In the December number of *Electrochemical Industry* for 1902 there appeared a paper by Townsend on "Sodium Chloride in Electrolytic Caustic Alkali" in which is discussed the function of this dividing partition or diaphragm, and what is termed in the article "the movement of undecomposed sodium chloride into the cathode compartment." The author notices that making due allowance for the water which is decomposed by the metallic sodium liberated on the cathode a concentration is effected in the cathode compartment. That is, the sodium chloride equivalent of the caustic soda found in the cathode liquor plus the salt still

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existing there as such gives an amount of sodium chloride far in excess of that in an equivalent volume of the original brine. This concentration effect Townsend accounts for as being "due in part to concentration of the cathode liquor by loss of water with the escaping hydrogen, in part to the cathodic reduction of hypochlorite and in part to the movement of the salt through the diaphragm under the influence of the difference of osmotic pressure upon opposite sides of the membrane." These explanations are insufficient to account for the observed facts. If provision be made for preventing any loss of water occasioned by the hydrogen escaping from the cathode compartment, this concentration effect is not appreciably decreased, and therefore this factor may be neglected in this discussion. When we consider that the hypochlorite reduced at the cathode had originally been formed at the expense of an equivalent amount of caustic soda it is seen that this reaction can add nothing to the net sodium chloride concentration. The diffusion of salt into the cathode chamber is, to so large an extent, offset by the passage of sodium hydrate in the opposite direction that this also cannot be an important factor.

It is necessary therefore to seek additional explanations for this observed change in concentration of the cathode liquor. The search is not a long one, however, for so soon as we consider the relative velocities of the ions transporting the electricity, a most important factor in the situation, which Townsend has entirely overlooked, becomes apparent, namely, ion migration.

Let us consider the construction usually employed in representing this phenomenon.

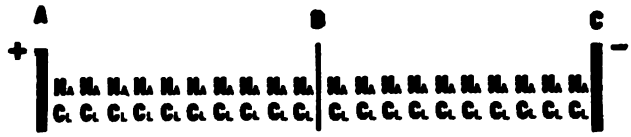

FIG. 1.

A and C are respectively the positive and negative electrodes of an electrolytic cell filled with solutions of salt, 10 molecules of which are shown on either side of D, the diaphragm.

Hittorf and others have shown that when concentrated solutions of sodium chloride are electrolyzed, about 65 per cent. of the total electricity passing through the solution is carried as negative elec-

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tricity by the chlorine ions and the remaining 35 per cent. as positive electricity by the sodium ions, *i. e.*, the relative ionic velocities are as 65:35. This fact has the following effect upon the concentration of the ions in the two compartments.

Under the influence of the drop of potential in the electrolyte 65 chlorine ions move up to the anode and away from the cathode in the same interval of time that 35 sodium ions move up to the cathode and away from the anode. The chlorine ions equivalent to the total current are discharged as gaseous chlorine, while at the cathode the corresponding sodium ions are set free and immediately react with the water, forming caustic soda and hydrogen. The change in concentration may be represented by

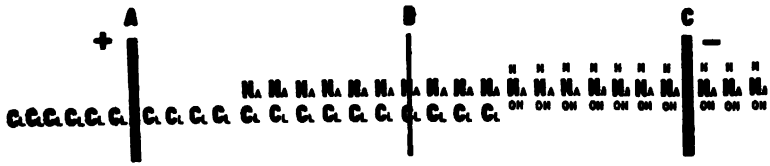

FIG. 2.

Ten atoms of chlorine are liberated at the anode and this compartment loses 3.5 molecules of salt. Ten atoms of hydrogen are thrown off at the cathode and the number of salt molecules in this compartment reduced by 6.5. But the total sodium ions have increased by 3.5 in the cathode and diminished by the same number in the anode compartment.

The change of concentration of the sodium ion in the cathode compartment so far as migration is concerned may be represented by the expression

$$\frac{dc_{Na}}{23} = \frac{C\,dt}{96540} N,$$

where N is the percentage of the total electricity which is transported as positive electricity by the sodium ions. If this quantity were constant we could calculate the composition of the cathode liquor when a given amount of sodium hydrate had been formed. But the moment that any caustic soda is present in the solution the hydroxyl ion takes a part in transporting the current. As its velocity is about 2.6 times as great as the chlorine ion the relative amount of the current which is carried as negative electricity is increased, and a proportionately smaller amount of sodium mi-

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grates into the cathode compartment. When the hydroxyl ion passes into the anode compartment it doubtless forms some hypochlorous acid which dissociates into the ions ClO and H. Inasmuch as the hydrogen ions move much more rapidly than the sodium ions the amount of positive electricity carried by the latter will therefore be still further decreased.

The rate of this change in the transport number of the sodium ion will vary as the concentration and dissociation of the caustic soda changes. In order to calculate the magnitude of this variation it is necessary to know the percentage dissociation of the sodium chloride and sodium hydrate in these concentrated solutions and the amount of hypochlorous acid existing in the anode compartment. These data are at present wanting.

The value of N for different concentrations of brine is given by Kohlrausch as follows:

Per cent. salt.	N.
5	0.363
15	0.354
24	0.350

That is, as the concentration of the salt solution decreases, the migration of the sodium ion into the cathode compartment is slightly increased.

In the ion migration therefore we find what is doubtless the most important factor in changing the relative concentration of salt in the two compartments.

The fact that the hydroxyl ions migrate with the negative electricity means that they must eventually pass through the diaphragm and be lost to the cathode liquor. While this loss decreases the rate at which caustic soda accumulates in the cell it has, however, no influence on the change of concentration of the sodium ion other than through the change in the transference numbers above referred to. Omitting for the moment the effect of diffusion due to osmotic pressure, which is small in any case, the difference between the caustic soda formed and that required by Faraday's Law is proportional to the current carried by the hydroxyl ions. Letting C_{OH} represent the total number of hydroxyl ions with the migration velocity V_{OH} and C_{Cl} the number of chlorine ions with .

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the velocity V_{Cl} the proportion of the negative electricity which is transported by the hydroxyl ions is

$$\frac{C_{OH}V_{OH}}{C_{OH}V_{OH}+C_{Cl}V_{Cl}},$$

and the increase in the amount of the caustic soda for the time dt is shown in part by the expression

$$\frac{dm}{40}=\frac{Cdt}{96540}-\left[\frac{Cdt}{96540}(1-N)\left(\frac{C_{OH}V_{Cl}}{C_{OH}V_{OH}+C_{Cl}V_{Cl}}\right)\right],$$

where $1-N$ is the proportion of the total electricity which is transported by the negative ions.

Although the presence of the unknown quantities make it impossible to quantitatively apply this equation, it serves to indicate the direction of the change introduced by varying conditions of concentration. Thus, for example, it is evident that in producing a given amount of sodium hydrate the current yield will more nearly approach the theoretical yield according as the initial concentration of the brine, and hence the term C_{Cl} is large. The limiting value of the left-hand member is also qualitatively shown, for inasmuch as the quantity $1-N$ increases with the number of hydroxyl ions, an increase in C_{OH} thus increases both the factors in the last term.

The influence of osmotic pressure of the solution in the two compartments may effect the changes in concentration of the electrolyte in two ways, depending on the degree of permeability of the diaphragm. If this dividing membrane be of such a nature as to restrain the osmotic pressure, water will pass into the more concentrated portion and thus dilute it. If the membrane be sufficiently porous, the partial pressures of all the particles will tend to be reduced and thus cause diffusion through the entire body of liquid. Inasmuch as commercial success demands a diaphragm of low electrical resistance the first effect may be safely neglected.

As we have already seen, for every 100 parts of salt decomposed by the current at the beginning about 65 per cent. is at the expense of the contents of the cathode compartment, and only 35 per cent. disappears from the anode chamber. If there is no brine flowing into the cell the anode compartment will become the most concentrated of the two in salt, and hence have the greater osmotic pressure. But as the caustic soda formed on the cathode increases more rapidly than does the difference in the salt content of the two

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compartments, the tendency for the caustic to diffuse in a direction opposite to that of the salt will overbalance the diffusion of the latter, and the cathode compartment will tend to grow more dilute.

Since osmotic pressure is proportional to the absolute temperature, this diffusion of the caustic soda may be decreased by maintaining the cathode compartment at a lower temperature than the anode compartment. In this way a higher current efficiency may be obtained than would be otherwise possible. In accordance with Soret's principle, the movement of salt from the anode side would at the same time be increased. The magnitude of this diffusion effect is, however, probably small when compared with changes in concentration due to the migration of the ions.

A third factor in changing the concentration of the two compartments is that known as electrical endosmose. By this action a solution is conveyed through capillary openings by the electric current. Such a mass of capillaries we have in our permeable dividing partition or diaphragm. The volume of solution moved is proportional to the total electrical transfer and to the dilution of the solution. It is probable that in concentrated solutions the change is not very great and except in certain types of cells this phenomenon plays an unimportant part.

Inasmuch as every electrolytic cell to be commercial must be continuous in its operation and must therefore be constantly supplied with brine, we have here a fourth factor in determining the concentration changes there taking place. Almost invariably the supply brine enters the anode compartment, passes through the diaphragm and flows from the cathode compartment as caustic effluent. Assuming this to be the case the effect of this flow of solution on the factors already mentioned is readily seen. The migration of the hydroxyl and chlorine ions will be more or less compensated by the movement of the liquid. This will result in decreasing the loss of caustic soda due to migration and also in reducing the amount of electricity carried by the negative ions. The velocity of the sodium ions will be correspondingly increased and the total effect will therefore be to decrease the concentration in the anode compartment and increase it in the cathode compartment.

The ordinary diffusion of the caustic soda will, of course, be also

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reduced, and the cathode concentration be still further increased.

If the supply of brine and the current strength be constant, an equilibrium in the composition of the caustic effluent will be reached. How far this composition will differ from that calculated from the equation

$$NaCl + xH_2O = Cl + NaOH + H + (x - 1)H_2O$$

will depend on the completeness with which the caustic soda formed is withdrawn from the active electrolyte and hence on the part played by the hydroxyl ions in carrying the electricity.

DISCUSSION.

DR. M. LOEB: Mr. Chairman, I would ask Dr. Walker whether he would not change the wording of his paper, in just one direction that I find very frequently misleading in these discussions. I do not think, under the conditions he mentions there, we could speak of an increase of concentration. In the original experiments we know very well that the anode substance is being continually furnished from the anode itself; that is to say, the anion is being continually furnished by the anode. In the case we are dealing with here, we really have a fall of concentration and not an increase of concentration. The relative fall of concentration will be naturally less around the anodes than around the cathodes, no matter whether the cathode be a large one or a small one; but the relative fall of concentration during electrolysis will be greater around the cathodes than at the anodes; and under those conditions it seems to me the matter cannot very well be considered otherwise, even if we wished to introduce questions of osmotic pressure. It really does not amount to a different phenomenon anyway. I think once you make it a question of fall of concentration rather than increase of concentration, the discussion will become very much simpler.

DR. W. H. WALKER: It depends entirely about what one is speaking. I was talking about the increase of the concentration of sodium ions in the cathode department. If the flow of liquor remains the same it means that the sodium increases in amount. There is no question about Soret's principle being an osmotic

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pressure phenomenon; but that is entirely distinct from the migration phenomenon. The diffusion due to osmotic pressure is one thing and loss due to migration is an entirely different thing.

I think it is shown now that if the rate of flow be rapid enough to compensate the migration velocity of the hydroxyl ion, there is no reason why one should not get 100 per cent. efficiency. All one has to do is to keep the hydroxyl from going backward.

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A paper read by title at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

THE INFLUENCE OF SOME IMPURITIES IN SALT UPON THE YIELD OF CAUSTIC SODA BY THE AMALGAM PROCESS.

By J. Wallace Walker, M.A., Ph.D., and Chas. S. Paterson, M.Sc.

In the following communication to the Society the authors do not wish to be understood as asserting that all or any of the sources of loss indicated by the results of the investigation are not already known to and provided against by the manufacturers in this particular department. The investigation was undertaken with an entirely different object than that conveyed by the title above, but as we have been unable to find any detailed statement in the literature of the subject regarding the effect of these impurities, we imagine that some of the results may not be without interest to those specially concerned with the commercial side of the problem, while some for which we have found as yet no satisfactory explanation have an interest which is more theoretical. The reason which induced us to make this series of determinations was the observation, during an illustrative experiment in which an impure sample of salt was subjected to electrolysis between a platinum and a mercury electrode, that hydrogen was evolved periodically from the surface of the mercury. On attempting to repeat the observation the necessary conditions could not be re-established. We were therefore obliged to make a detailed examination of the influence of such impurities as might have been present when the phenomenon was observed. This seems finally to have led to the desired result, but our deductions regarding it are reserved for a future communication.

Experiments were first made upon several samples of "chemically pure" salt, then upon two samples of commercial table salt labeled 'Morton' and 'Crosse and Blackwell,' and finally upon admixtures of these with very small quantities of various salts.

The apparatus employed is illustrated in the following diagram.

The electrolytic cell consisted of a glass tube about 30 cm. in

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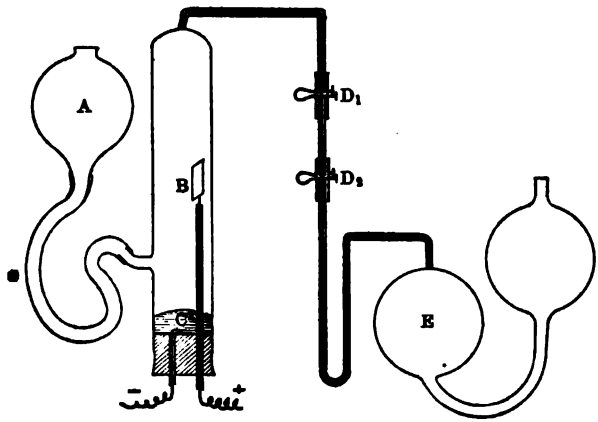
length and 2.1 cm. internal diameter. The top of it terminated in a capillary tube, through which the gases evolved during an ex-



periment could be driven by raising the reservoir A and opening the pinch-cock D into the gas pipette E. The lower end of the cell was closed by a rubber stopper through which passed two glass tubes carrying platinum wires. One of these ended immediately above the stopper and served to make connection with the mercury cathode C, while the other was prolonged upwards and ended in a platinum anode B of about ½ square inch surface. The same measured volume of mercury, weighing 67.6 grams, was placed in the cell for each experiment, and an almost saturated salt solution containing about 330 grams per liter was made up for each set of experiments. When making an observation the mercury was first placed in the cell, then the 200 cc. of salt solution, which were necessary to fill it, and a current of 0.5 ampere were allowed to flow for 15 minutes, the cell being meantime covered with a black cloth to prevent combination of the hydrogen and chlorine. The gases consisting of a mixture of chlorine, hydrogen and possibly some oxygen were then immediately transferred to a gas pipette containing 25 per cent. caustic potash by which means the chlorine was removed, then to a second containing alkaline pyrogallate, where the oxygen was absorbed, the residual volume of hydrogen which was measured representing the loss of caustic soda in the experiment. The source of current was the 110-volt lighting circuit, and the cell was placed in series with one 16 c.p. lamp, or with

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several such lamps arranged in parallel when a higher current density was required. The current which was measured by an ordinary Weston ammeter was very constant during a single experiment, but varied on different days from 0.47 to 0.52 ampere. Since the internal diameter of the cell was 2.1 cm. and the external diameter of the anode tube which passed through it 0.55 cm., the free surface of mercury exposed to the electrolyte measured 3.21 sq. cm., which, with a current of 0.5 ampere, is equivalent to a current density of 15 amperes per square decimeter. This seems to be nearly the same value as that employed in the commercial process. After each determination the cell was washed out very carefully with dilute hydrochloric acid and water.

Experiments were first made with three samples of salt in which no impurities could be detected by analysis. The results were as follows:

Source of salt.	Hydrogen evolved, cc.	Loss. Per cent.
Harrington Bros.....	0.8	1.4
" "	0.9	1.6
Merck, I.....	0.9	1.6
"	0.9	1.6
Merck, II.....	0.8	1.4
"	0.8	1.4

The figures in the last column represent the percentage loss from the theoretical amount. They show that with pure salt the loss is in no case greater than 1.6 per cent. The volume of gas given off by the chemically pure salt was found in a large number of experiments to be quite constant. It was therefore deducted from all subsequent readings, so that the percentage loss calculated with the impure salt is that due to the impurity alone. During the course of the experiments which follow, whenever a fresh sample of mercury had to be used as well as at other frequent intervals, blank tests were made with pure salt solution as control experiments, and this value of the cell-error was found in all cases to be constant. One of the main objects of these blank tests was to determine whether or not the mercury contained any metallic impurity, such as iron, which would affect the yield.

Two samples of commercial table salt were examined. The first labeled "Crosse and Blackwell" was found on analysis to contain some Ca, some SO_4, and traces of Mg and K. This gave the fol-

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lowing result: Volume of H 0.3 cc., per cent. loss 0.5. The second labeled "Morton" was found to contain 0.3 per cent. Ca, and a very indefinite trace of Mg, as well as SO_4. It gave a result identical with that of chemically pure salt.

The first impurities whose influence was examined were those which commonly occur in natural salt. The method employed for adding a known amount of an impurity was to add the requisite volume of a standard solution of the impurity to the 200 cc. of salt solution required to fill the apparatus. In the first table the results obtained for the addition of small quantities of K, Ca, Mg, and Fe to pure salt, are given. The K was added as KCl from a solution containing 19 grams KCl in 100 cc.; the Ca as $CaCl_2$ from a solution containing 9.1 grams Ca in 100 cc., the Mg was added as $MgSO_4$ from a solution of 41 grams $MgSO_4.7H_2O$ in 100 cc.; and the Fe as $FeCl_3$ from a solution containing 0.63 gram Fe in 100 cc. The first column in the table contains the number of the experiment, the second the amount of impurity expressed in grams of its metallic constituent which have been added to 200 cc. salt solution, the third the volume of H evolved, and the fourth the percentage loss calculated from this.

TABLE I.

No.	Impurity.		Hydrogen. cc.	Loss. Per cent.
1	0.10	K	0.59	0.0
2	0.0455	Ca	0.98	0.1
3	0.1696	Ca	2.26	2.5
4	0.017	Mg	1.47	1.04
5	0.17	Mg	0.0	0.0
6	0.00063	Fe	1.18	0.5
7	0.00126	Fe	1.18	0.5
8	0.00189	Fe	2.06	2.2
9	0.00315	Fe	2.16	2.34
10	0.0063	Fe	2.00	2.1

These four represent the common impurities in commercial salt, and the fourth column shows that up to the limits employed at least their influence is very slight. The amounts of impurities present, however, are so small that they may be characterized as mere traces. Most of the experiments were repeated several times with results which showed an agreement within the error of reading of the hydrogen evolved.

It was next thought desirable to try the effects of nickel and cobalt, which although not impurities commonly occurring in natural salt, are very closely related to iron in their general proper-

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ties and behavior. The nickel was added as $NiSO_4$ from a solution containing 0.45 gram Ni in 100 cc., the cobalt as $Co(NO_3)_2$ from a solution containing 1.83 grams $Co(NO_3)_2$ in 100 cc.

TABLE II.

No.	Impurity.	Hydrogen. cc.	Loss. Per cent.
1	0.00022 Ni	1.67	1.5
2	0.00045 Ni	6.23	9.5
3	0.0009 Ni	5.92	9.0
4	0.0022 Ni	9.39	15.3
5	0.0045 Ni	16.1	27.8
6	0.0067 Ni	17.6	30.4
7	0.009 Ni	18.8	33.1
8	0.0135 Ni	20.3	35.8
9	0.00059 Co	1.37	0.9
10	0.0059 Co	13.43	23.1

The results obtained with nickel are very surprising when compared with those obtained with iron at similar concentrations. Whereas 0.0063 gram Fe causes a loss of only 2 per cent., the same amount of nickel causes a loss of 30 per cent., and this when it is present in the ratio of 1 part to 10,000 of salt. Also, while the effect of iron does not increase appreciably when its amount is trebled as seen in Nos. 8 and 10, Table I., that of nickel becomes doubled for the same change in concentration, *vide* Nos. 4 and 6, Table II. Although only two experiments were made with cobalt they seem to indicate that its behavior is similar to that of nickel.

In the preceding experiments the impurities were added to a solution of chemically pure salt, and the influence of some of them, *e. g.*, iron, was not great. When, however, a small quantity of a solution containing iron was added to a sample of commercial salt already containing traces of calcium and magnesium, very different results were obtained. The first two results in Table III. were obtained with "Morton's," the remainder with "Crosse and Blackwell's" salt.

TABLE III.

No.	Impurity.	Hydrogen. cc.	Loss. Per cent.
1	0.00063 Fe	6.74	10.4
2	0.00063 Fe	12.65	21.7
3	0.00063 Fe	18.4	30.3
4	0.00063 Fe	9.1	13.4
5	0.00126 Fe	17.1	27.5
6	0.00252 Fe	18.1	29.3
7	0.0032 Fe	16.9	27.1
The current was then doubled.			
8	0.00063 Fe	48.98	50.7
9	0.00126 Fe	46.33	45.0
10	0.00252 Fe	35.6	34.6
11	0.0032 Fe	29.2	27.7

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From this table it appears that the addition of an almost undetectable trace of iron (the proportion of Fe to NaCl is as 1 : 100,000) is sufficient to cause a loss of as much as 30 per cent., and it does not increase much with the concentration of the iron. If, however, the current density is doubled, the loss is almost doubled for the smallest trace of iron added, and decreases with an increase in concentration of the iron. These results seem to show that, although a single impurity present in very small amount may have little effect on the yield of caustic soda, its influence may be enormously increased if another impurity be present at the same time. The first four determinations in the last table give the first indications of an anomalous behavior which was subsequently observed in a more pronounced degree in the case of nickel. With the particular concentration of iron employed in them it was found impossible to obtain the same result in two consecutive experiments, although the conditions seemed to be exactly the same. The appearance of the mercury cathode was different in all four. Hydrogen was evolved from the start in all of them, but it died down and became more vigorous again when a solid deposit formed on the surface of the mercury. The formation of this solid took six minutes in No. 1, four minutes in No. 2 and only two minutes in No. 3. The amount of hydrogen evolved is evidently greater the longer this solid is on the surface of the mercury, but we can give no explanation of its more rapid formation in one experiment than in another.

A series of experiments were then made with the object of determining which of the impurities usually present in commercial salt has most influence upon the yield in the presence of iron. The salt used was "Merck's" and small quantities of potassium, of magnesium, and of calcium salts were added in the presence of ferric chloride. The results are contained in Table IV.

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TABLE IV.

No.	Iron added.	Impurity.	Hydrogen. cc.	Loss. Per cent.
1	0.00063	0.17 K	0.79	0.0
2	0.00063	0.0085 Mg	7.35	11.9
3	0.00063	0.017 Mg	6.23	9.5
4	0.00063	0.034 Mg	3.43	4.9
5	0.00063	0.06 Mg	4.41	6.4
6	0.00126	0.0085 Mg	8.57	13.9
7	0.00252	0.0085 Mg	8.57	13.9
8	0.00504	0.0085 Mg	11.37	18.8
9	0.01008	0.0085 Mg	12.6	19.8
10	0.00063	0.0424 Ca	4.61	6.8
11	0.00063	0.0848 Ca	10.59	17.7
12	0.00063	0.1696 Ca	12.75	20.0
13	0.00126	0.0424 Ca	4.61	6.8
14	0.0063	0.0424 Ca	13.43	22.9

Experiment No. 1 shows that potassium even when present in considerable quantity has, as might be expected, no effect. Nos. 2, 3, 4, 5 and 6 show when compared with those in Table I. that although iron and magnesium separately give a loss of only 0.5—1 per cent., when both are added together in the same quantities as before the loss is increased about ten times. Nos. 10, 11, 12, 13, and 14 show that the same is true for iron and calcium. These results also explain the large losses observed when iron is added to the commercial salts which were found on analysis to contain both calcium and magnesium. Nos. 2, 3, 4 and 5 show an indication of the same discrepancy as was observed in Table III. with the same amount of iron, and the same phenomena were observed at the surface of the mercury. In this case however the differences may be due to the varying amounts of magnesium present.

As nickel alone has been found to give such remarkable results, it seemed desirable to observe its effect in the presence of calcium and magnesium also. The results with magnesium are contained in Table V., those with calcium in Table VI.

TABLE V.

No.	Nickel added.	Impurity.	Hydrogen. cc.	Loss. Per cent.
1	0.00058	0.0085 Mg	3.92	5.5
2	0.00058	0.017 Mg	3.04	3.9
3	0.00058	0.6 Mg	3.14	4.1
4	0.00116	0.0085 Mg	5.82	8.9
5	0.0029	0.0085 Mg	6.43	10.0
6	0.0029	0.017 Mg	5.41	8.4

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These results show that for a constant amount of nickel the loss varies but slightly with the amount of magnesium present, while with a constant amount of magnesium the loss increases rapidly with an increase in the quantity of nickel. This is in agreement with what was found before for nickel alone.

TABLE VI.

No.	Nickel added.	Impurity.	Hydrogen. cc.	Loss. Per cent.
1.....	0.00058	0.091 Ca	4.9	7.6
2.....	0.00116	0.091 Ca	9.7	16.4
3.....	0.0017	0.0455 Ca	25.51	45.8
4.....	0.0017	0.0455 Ca	5.41	8.3
5	0.0017	0.0455 Ca	41.96	75.3
6.....	0.0017	0.0455 Ca	8.98	15.5
7.....	0.0017	0.0455 Ca	34.5	60.9
8.....	0.0017	0.091 Ca	10.2	17.5
9.....	0.0017	0.091 Ca	10.2	16.2
10.....	0.0017	0.091 Ca	10.0	15.9
11.....	0.0017	0.091 Ca	8.68	13.5
12.....	0.0017	0.1456 Ca	19.3	34.5

These results show that the amount of hydrogen evolved increases rapidly with the amount of both nickel and calcium present. The same anomaly observed in the case of iron is met with here, but in a far more pronounced degree. Whereas experiments 8, 9, 10 and 11, which were performed with the same concentrations and approximately the same current density, gave results in fairly close agreement, experiments 3 to 7, which were performed with the same amount of nickel and half the amount of calcium, gave results varying from 8 to 75 per cent., although the current density and all other conditions were, as far as could be observed, practically the same. We are unable to offer any explanation of this phenomenon.

The amalgam formed when chemically pure salt was used, showed no immediate signs of decomposition in the cell when the current was turned off; when iron was present, decomposition was immediately noticeable, and when nickel, either alone or with other impurities, was present, the decomposition commenced instantly and was very rapid. Some measurements were made of the amount of hydrogen evolved from the amalgam during the fifteen minutes after the current was turned off. In every case the current had been flowing for fifteen minutes. With pure salt the vol-

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ume of hydrogen was not measurable. With pure salt containing 0.00315 gram of Fe in 200 cc., 2 per cent. of the hydrogen represented by the current was liberated. The other experiments quoted refer to Table VI. and are designated by their numbers:

No.	Hydrogen. Per cent.	No.	Hydrogen. Per cent.
3	29.4	7	19.7
4	68.6	8	57.2
5	14.4	9	52.9
6	62.7	10	57.8

These results are of interest in connection with a process which has been recently proposed (*J. Soc. Chem. Ind.*, 21, 125) for the rapid extraction of the sodium from the amalgam. The essence of the method seems to consist in placing the amalgam in contact with water and carbon upon which a metal has been electrolytically deposited. If the metal thus used be either iron or nickel it will certainly be efficient, but it will involve the purification of the whole of the mercury before the latter can be again employed in an electrolytic cell.

It is difficult to believe that local galvanic action is alone responsible for the results obtained with iron and nickel. In the first place because the amount of either of these which can actually find its way into the amalgam is infinitesimal. For, although 1 or 2 parts are added to 100,000 of salt, only the iron or nickel in the immediate neighborhood of the mercury has an opportunity of reaching that electrode, the remainder must be rapidly converted into hydroxide by the caustic soda produced. In the second place the influence of nickel is far more pronounced than that of iron and yet they stand very close together in the electrochemical series. However, we have observed by rough measurements that whereas iron and nickel show almost no potential difference in salt solution, iron shows a considerably higher electromotive force when placed against pure sodium amalgam in salt solution than nickel shows under the same conditions. A possible explanation of their remarkable power of decomposing sodium amalgam which we would offer is based on the observation very often made during the course of these experiments that the surface of the mercury became coated with solid or semi-solid material at far lower concentrations of magnesium when nickel or iron was present, than in their absence. It seems as if the metals capable of decomposing

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water may unite with the Fe or Ni in the mercury to form a compound which can decompose water more readily than the pure sodium amalgam can. These results seem to have a further interest from their bearing upon the general question of the influence of impurity in a metallic electrode, regarding which our ideas seem at present to be in a somewhat unsatisfactory condition. In this connection we propose to pursue the inquiry further.

The results obtained seem to indicate that with a chemically pure salt the amalgam process should give an almost theoretical yield, and that with a salt containing small quantities of the impurities common to natural salt, such as calcium, magnesium or potassium, the loss would be very small. If, however, in addition to these the cell should become contaminated with the minutest traces of iron salts, such as might be produced by the action of the chlorine on any iron or iron compounds in the apparatus, the effect may become so great as to render the plant useless.

CHEMISTRY AND MINING BUILDING,
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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, President Richards in the Chair.

CORROSION OF METALS BY ELECTROLYSIS.

By A. A. Knudson.

The corrosion of metals by electrolysis caused by electric currents *under control,* has been known since the discovery of those most useful inventions, the voltaic cell, and the electroplating bath; the generation and flow however of unintentional currents (if we may so call them) due to defects in certain mechanical constructions, or systems of operating, are often responsible for serious results in the corrosion of metals, and although this subject has a very wide range, it may be considered with profit even in the limited time devoted to an ordinary paper and its discussion. Your attention is therefore first invited to a few instances of corrosive effects from unintentional electric currents such as are met with in practice, and later, considerations for their avoidance.

Part I.—Galvanic action between dissimilar metals, causing corrosion.

Part II.—Destructive effects of railway currents upon subterraneous metals. Historically the first currents of electricity ever generated by chemical action were probably among the dissimilar *metallic ores* deposited in the earth. Such currents have long been known to exist, and probably have existed since the world was made. An instance illustrative of the movements of earth currents happened in the experience of the writer some years ago. In grounding a telephone line at a mine in Nova Scotia, where gold, iron, copper, and other metals were present, an earth current was discovered upon the line, of such strength as to prevent the use of the magnetic signal bells. The "ground" at the mine had to be moved a quarter of a mile before relief from these currents were obtained and the line made to work.

Instances have often been found where dissimilar metals placed close together in the construction of vessels, where sea water is accessible, result in corrosion due to galvanic action; if as usual the metals are iron and copper (or alloys of copper) the iron or

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steel, which is electro-positive, suffers the most. An examination made of a copper-plated ocean tug some years ago, may be cited as an illustration. This vessel which had been plated about four years previous to our examination, had been in constant service during that time in the harbor of New York and other places; had changed owners two or three times; had been aground according to the statement of the engineer about a dozen times and in some cases upon the rocks. We found after the boat was placed in dry dock, a number of iron patches bolted over the copper plating at various places on the hull where repairs had been necessary, and at other places iron bolt heads were found against the copper attached to rods which came through the hull securing or supporting machinery upon the inside; in short after the vessel had left the control of those who plated her, there seemed to be no one on the boat who understood the effect, if the iron of the hull became exposed. Under such circumstances it was not surprising that corrosion had been active, the bolt heads upon the patches as well as the other places were nearly gone, and wherever the iron of the hull was exposed, evidence of electrolysis was found. One point however seemed perfectly clear, and that was, of the several hundred square feet of copper plating intact, there was no evidence whatever of any corrosive action upon the iron under the copper, which was examined by cutting through with a file in several places.

Another case of sea-water corrosion due to placing together dissimilar metals, is the galvanic effect upon the propeller shafts of steamers. A brief description of the tail shafts as they are termed will be necessary in order to explain clearly this effect.

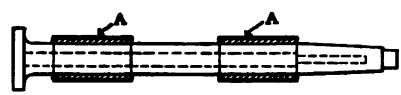

FIG. 1.

Referring to the sketch, Fig. 1 represents a tail shaft of steel with the usual hollow centre, and tapered at the end for the propeller, at the opposite end a flange is provided for bolting to the other portion of the shaft; at points A, A, are placed what are called the "liners;" these are usually constructed of brass or bronze, shrunken on the shaft, and further secured by rivets; these liners are the bearings and revolve upon a surface of *lignum vitae* which is placed entirely around the liners in the form of

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strips or bars which are held in place by a water-tight iron case; salt water has access to the interior of this case, and usually there is no other lubrication.

The effect of this construction is that galvanic action takes place between the brass or bronze liners and the steel shaft, the result, as one has described it being "annular nicking" of the steel shaft, which in a number of recorded instances has been shown to cause cracks, and finally a break, resulting sometimes in the loss of the propeller, the consequent danger of the lives of passengers, and great financial loss to the owners of the ship. One case is given as an illustration, the account being taken from *Marine Engineering*, November, 1901. The engineer of an English steamer noticed water dripping from the central hole in the after crank shaft, and believing it coming from a fissure in the tail shaft, the same was removed when in port and examined. The shaft was taken to the factory, placed in a lathe, and a light cut taken over the surface which was covered by the liners or sleeves. These were of brass, shrunk and riveted on, and were 3 feet long. The account goes on to say, "Corrosion was found at all of the liner joints, but the worst was at the joint of the two end sleeves. At this point a cut was made three-eighths of an inch wide by seven-eighths of an inch deep to learn to what depth corrosion had gone. Through the center of the crack through a rivet hole a long cut was made by a planer which showed the crack extended 1¾ inches below the surface."

The shaft had been in use but nine months.

Analysis of the materials were made before the shaft left the factory, and upon its return.

Samples taken from the shaft and tested for tensional stress, elastic limit, and elongation, showed them to be practically the same as they were when they first left the factory.

"An analysis of the brass sleeves showed the alloy to be as follows:

	Per cent.
Tin	9.21
Copper	86.65
Lead	0.08
Zinc	3.89

"The account further states that this high percentage of copper was doubtless one of the reasons for rapid corrosion, as it is found

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that galvanic action proceeds more slowly when the brass contains only 45 to 50 per cent. of copper."

The report of the experts who examined this shaft was that the "failure was, by detail, hastened by annular nicking caused by corrosion arising from galvanic action set up by the sleeves."

There have been many other accounts—some of them no doubt will be recalled by this case—where corrosion by electrolysis has been the cause of the loss of propellers, but we think this one reference is sufficient to show what dire results this apparently "little thing" is responsible for.

Another phase of this subject came under our personal notice during an examination in a city for electrolysis of water pipes; our attention was called by the Superintendent of Water Works to several *water meters* which he believed had been ruined by electrolysis caused by railway currents. After making careful tests at locations where these meters had been in use, and not finding any signs of railway current, we had one of them taken apart for closer inspection. We found in the interior a *brass valve* arranged to move over iron slides, the slides being a part of the iron frame of the meter; suspecting galvanic action, we made an effort to measure the voltage, and selecting a meter that was not so damaged as to entirely prevent its working, we connected the brass valve with an insulated wire leading it out through the discharge, thence to the millivoltmeter; another wire from the iron casing was connected to the opposite pole of the instrument; we then turned on the water from a service tap and allowed the meter to work the same as in practice; the effect was instantly shown upon the millivoltmeter which registered from 0.004 to 0.008 volt; variations of the needle between the minimum and maximum were caused by the variation of contact between the brass valve and the iron guides, over the uneven surface; the water was slightly brackish. The iron case was positive to the brass valve; the interior iron parts were softened and broken away. The number of this meter was taken, and the records in the office of the Water Department examined to see how long it had been in use, which was found to be about twelve years; from this data we make the following deduction. A water meter or other like instrument constructed with dissimilar metals such as brass valves running upon iron guides, in brackish water with an average difference of

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potential of 0.006 volt, will in twelve years be ruined by electrolysis due to galvanic action, and register inaccurately in a much shorter period. It is but proper to say that water meters of this construction have long since been changed by the manufacturer, and those now made by the same firm are differently constructed and are not liable to galvanic action in their working parts.

Other instances of the use of dissimilar metals in various other constructions could be mentioned, such as in steam plants, but we assume that sufficient has been said to at least call attention to the evils which may result from the use of dissimilar metals in contact with liquids, wherever they may be placed.

In regard to electrolytic corrosion of metals caused by electricity from a source foreign to themselves, or similar in action to the electroplating bath, we are again dealing with the vagrant but destructive currents of which perhaps the most familiar are those causing corrosion of underground pipes by railway currents. Before passing to underground mains however we will briefly refer to a case discovered last summer which may be of interest as showing the effect of electrolytic action upon the metals of bridges that are above the surface of the ground, as illustrated in Fig. 2. During an investigation in an eastern city, the Superintendent of Bridges called our attention to the rapid corrosion of some of the shore spans of one of the bridges, where the heavy planks of the roadway lay nearly against them, there being a space of about one-fourth of an inch between; in this space there had been lodged the sweepings of the bridge, a material composed mostly of animal refuse containing such chemical ingredients as would furnish a convenient electrolyte when wet. At the foot of one of the spans where the worst corrosion was found, a test with a millivoltmeter showed the iron span positive to the surrounding earth with a difference of potential of from 0.05 to 0.06 volt. With a view of finding the point of entry of this current a test was made at each of the four iron cylinder piers which supports the bridge, and stand in the river bed. At the one nearest the most injured span a difference of potential of from 0.3 to 0.5 of a volt was found with the water positive to the pier, and none to speak of at the other three piers. These piers connect with the iron of the bridge.

The metal of the span which was originally three-eighths of an

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inch thick was eaten through in three places; two of the holes are shown in the photo, the third was discovered after the picture was taken; near these holes and extending for a considerable distance to the right, the metal was thinned down to about the thickness of writing paper; the other three spans were examined but only slight corrosion was found, and no readable difference of potential between them and the earth. The tracing of the trolley current to the pier, and thence to the bridge, and out from the span to the earth, through the soil spoken of, offers opportunity for galvanic action, which we believe was the principal cause for the corrosion discovered at this point.

PART III.—A brief historical résumé will first be given as to the results of a few surveys and tests made during the past few years in the City of New York, concerning effects upon underground structures.

In the spring of 1897, the writer discovered, while making an electrical survey in Manhattan in behalf of one of the railway companies, that a portion of the returning railway currents generated at the Kent Avenue Power Station in Brooklyn, E. D., passed over the New York and Brooklyn bridge to underground pipes in Manhattan. Refer to map, Fig. 3. At that time it was supposed that these currents took the shortest and most direct path through these pipes back to Brooklyn, taking the river in the vicinity of Grand Street, about opposite the power house which is located on the water front in Brooklyn at Kent and Division Avenues.

In October, 1898, while making further measurements on the bridge practically the same electrical conditions were found; *viz.*, currents from Brooklyn flowing over the bridge and down the pillars in Park Row, which support the terminal structure and the elevated railway station, and from them to water and gas pipes in the street.

In the early part of the following year (1899) Mr. Charles R. Barnes, electrical expert for the New York State Railway Commissioners, made at their direction an extended survey through the Borough of Manhattan, and found the electrical conditions at the bridge and other points in the city practically the same as we found them in 1897 and 1898.

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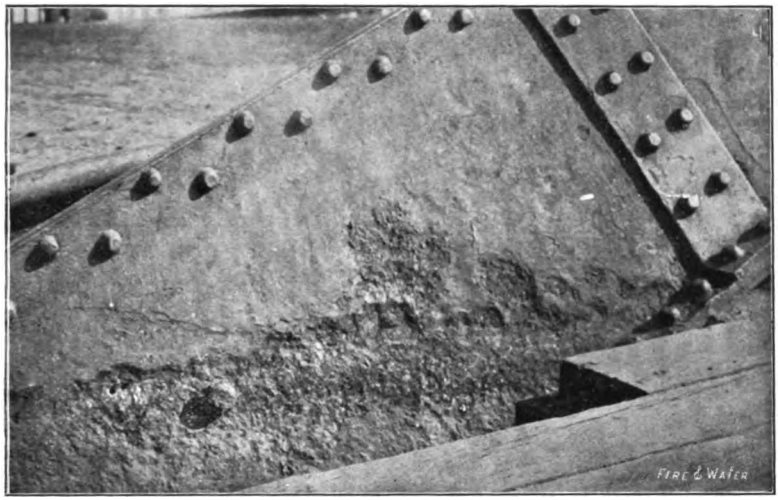

FIG. 2.

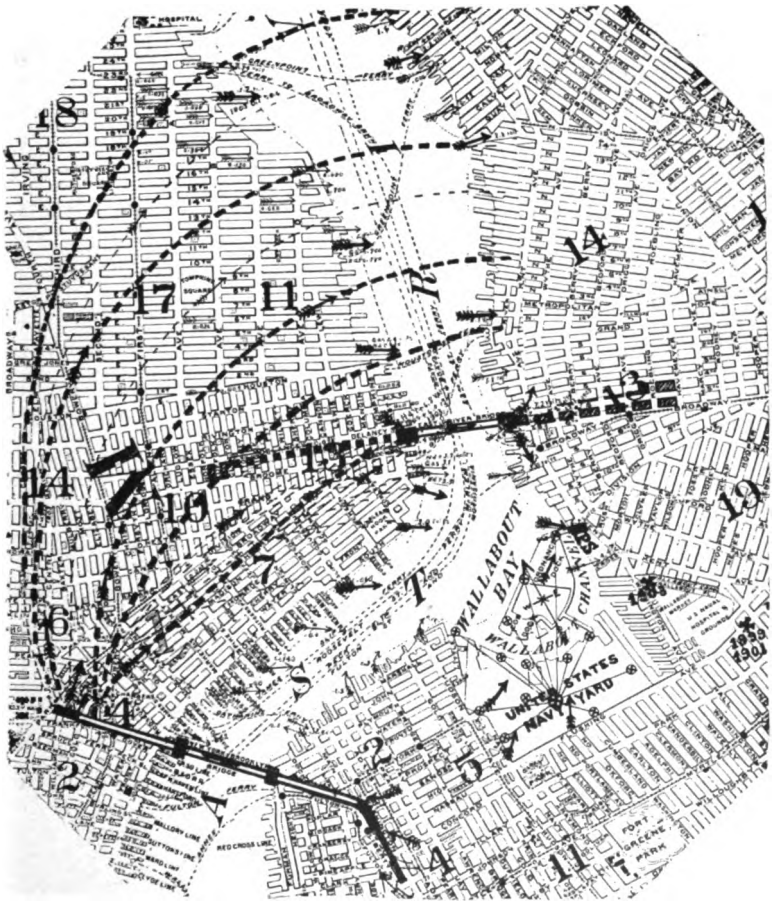

FIG. 3.—Map showing results of electrical measurements in boroughs of Manhattan and Brooklyn, New York City. March, 1897; October, 1898; May, 1902; March, 1903. Arrows indicate direction of returning railway currents. Figures, maximum voltmeter readings.

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In the month of May, 1902, in the interests of parties engaged in a lawsuit, a further survey was made by the writer in this section of the city, for the purpose of ascertaining if there were currents of electricity flowing through underground pipes, what direction they were taking, and their identity and source. It was discovered, as will be seen by the direction of the arrows and curve lines upon the map, that a portion of the Brooklyn railway currents generated at the Kent Avenue Power Station, in their return to that station pass over the New York and Brooklyn bridge to Manhattan, thence flow through underground pipes as far North as 23rd St., and flow *east towards the river* through pipes in streets running east and west, and also returning over the *new East River bridge.*

On the Brooklyn side of the river the currents were found to be *leaving the river,* and passing into the underground pipes as far north as Greenpoint at about opposite 23rd St., Manhattan, thence flowing south to their starting point, the power station in Kent Avenue.

One means of identifying this trolley current was by a test during the so-called rush hours between 5 and 7 o'clock in the evening, at the foot of 21st St., between a pipe connecting with the gas mains, and the *river,* the rise in voltage indicated when the cars are carrying the heaviest load, a little before and after 6 o'clock, and the falling off as the load becomes lighter.

The same test was made between one of the pillars at the Manhattan terminus of the bridge and a water pipe, on the following evening, where the maximum difference of potential was 3.6, this also at the same time as the previous test.

Potential readings through the streets were obtained by connections between gas posts upon the gas mains, and between hydrants on the water mains with the millivoltmeter. A higher reading instrument was used for other tests. A few *current readings* were made upon pipes found exposed in the subway in Elm Street. In 1902, 5.9 amperes were found flowing north upon a 12-inch pipe near Grand Street. This year we find the 12-inch main has disappeared and no comparative test could be made. Upon a 20-inch main, however, a little north of Canal Street, we find 6 amperes flowing north; this however is only a portion flow-

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ing north as it was found that current is passing through the metal of the subway as well. One point of contact between this 20-inch main and subway metals was discovered where a hub of the main rests against a girder just north of this point. On the other, or south side of Canal Street we could get no reading, the cause being that this main came to a dead end about a block below; beyond the dead end for about half a block the main had been removed, current therefore passing north from the bridge by way of the metal work of the subway; thence just above Canal Street 6 amperes of it is transferred to the 20-inch main; how much more is passing through the subway structure cannot be ascertained, but the most of this same current we have no doubt finds its way through subway metals and pipes to, and over the East River bridge, while a smaller amount is spread through the pipes and passes by way of the river bed to the power station. The maximum readings a year ago between a hydrant and the structure were 5.4 volts; now they are 6.5 volts and 6 volts from the gas mains. On the Brooklyn side, the test a year ago was 7.2 volts. Direction of flow *from bridge to pipes;* this year the reading was only 0.5 volt. The reason for this much lower difference of potential than last year on the Brooklyn side was owing to the conditions being changed, *viz.*, a 6-inch wrought iron pipe is now led up to, and rests upon the steel girders of the roadway, making a fairly good connection between the bridge structure and the water piping of the borough.

This pipe supplies the engines upon the roadway with water. A current measurement (using the "fall of potential method") was taken upon that portion of this pipe which is close to the ground, and a maximum flow of 69.5 amperes was found passing off the bridge through this medium to the Brooklyn mains. This current flow was determined later by a test at Columbia University upon a pipe of the same size. This *current* found entering the mains in Brooklyn must again *leave them* in its course to the power house, and it is well understood that at such points where the current passes into the soil, electrolytic corrosion of the iron occurs.

Further tests between the structure and pipes in Brooklyn were as follows: about one block from the river, difference of potential 2 volts, bridge positive to mains. Two blocks from the river, 2.5

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volts, same direction of current. These latter tests indicate that by no means is all of the current which passes over the bridge to Brooklyn, which is considerable, passing through the 6-inch pipe, that is but *one outlet;* other outlets are such parts of the metal structure as may connect with the earth, where the resistance is sufficiently low, and at such places corrosion is possible.

The new bridge is therefore taking the larger portion of straying railway current which formerly passed through the underground pipes in Manhattan to the north, or in other words it is in such position that it invites a more direct return path for these currents to flow back to the Brooklyn Power Station. This new return path will continue to improve as a conductor, as the bridge nears completion, when more current will be diverted in this direction, unless some method is devised to control it; the readings taken this year were made *after the roadway had been joined,* which may account largely for the increased flow indicated over last year.

It has been known for some years that pipes in the Navy Yard have been destroyed from time to time, by electrolysis, evidence of which we have seen in a number of samples shown us during recent visits.

A convenient method for taking potential measurements in the Navy Yard is shown upon the map and in larger scale in Fig. 4. Wires have been run from a central station connecting with the water mains at different points; by this method the difference of potential can be taken between any two points in the system—there are fourteen of these connections. The direction of the railway currents are always towards the power station, which is located just across the channel from the cob dock. The most of the pipes which have been destroyed were in the cob dock. At one time it was feared that the steamship "Columbia" used as a receiving ship was being damaged on account of being in line of these currents, but we are reliably informed that the plates of this ship were carefully examined when the boat was recently in dry dock, and no action except what might be expected from sea water corrosion was discovered. The difference in potential now between points on the sides of the yard near Flushing Avenue and Navy Street, to the point nearest the power station, is 20 to 25 volts; formerly it was higher than that.

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The railway company suggested that the damage caused, and being caused, to the pipes underground was not due to their currents, but was caused by the Navy Yard's own electric light and power circuits, whose large plant is in operation.

While the officials were morally certain that the currents causing damage were from the Railway Power station, the question remained uncertain until the day of the late President McKinley's funeral, when the Kent Avenue Power Station as well as all others in the country closed down for five minutes.

It occurred to some of the engineers of the yard that it would be a good plan to make a few tests at that time, and while the lighting and power circuits were running, and the Railway Power Station closed down, this was done. It was found that the voltmeter needles *remained at zero* at every test that was made, proving conclusively that the currents causing the damage emanated from the Railway Power Station.

Several water and gas mains have burst in Brooklyn, owing to electrolysis. We will, however, refer only to those of which a record has been kept in the section of the city we have been considering. Two views will be shown, the only ones photographed so far as known. Fig. 5 represents an 8-inch water main which burst in Flushing Avenue, near Classon Avenue, near the Navy Yard Hospital grounds, July 14th, 1899, as shown by the records of the Water Department.

All the characteristics of electrolysis were found upon this section of pipe, *viz.*, the soft state of the iron in several places which was reduced to a condition of graphite, easily shaved with a pocket knife. The voltmeter readings which we took from where this pipe was removed showed it positive to the rails; besides it was resting in wet soil. The pipe from which this sample was taken was of the Scotch iron make, which is identified by the bulging rings found on every length; they are from 3 to 4 inches wide; one of these rings can be seen at the left of this section; this make of pipe is further identified by the lengths being 9 feet instead of 12 feet. The hub is also deeper. Subsequently to the bursting of this main at this point, there have been three other failures upon the same pipe in this street within short distances from each other; according to the records there was a failure on March 13th, 1901, one on June 25th, 1901, and another on November 7th, 1901. Two

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FIG. 4.—Navy Yard, showing points where test-wires are connected with mains, and location of power house. Arrows show direction of railway currents through mains.

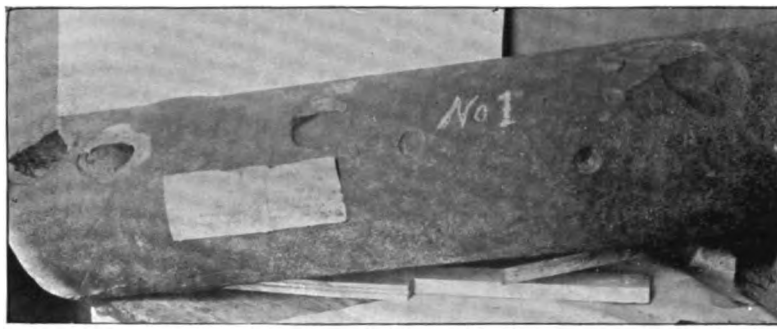

FIG. 5.

FIG. 6.—Section of 6-inch cast iron water main destroyed by "electrolysis," removed from Wallabout Place, east of Washington Avenue, Brooklyn, N. Y., January 21, 1903.

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of these damaged sections we have not seen, but we are informed by the men who removed them that the iron was in practically the same condition as to holes and soft spots as the sample shown in the photo. There is no doubt therefore that all of these four failures were caused by electrolysis. The next photograph we will show is represented in Fig. 6.

This is a 6-inch pipe, and, as you may readily see, represents a clear case of electrolysis. This was taken from Wallabout Place, near Washington Avenue, a short distance from the canal. This pipe was positive to rails on Washington Avenue, positive to canal, and positive to gas main in same street. The highest reading found was 5.9 volts to rails.

A few years ago an impression prevailed to some extent, that underground mains in Brooklyn were immune from electrolysis. Some gave as a reason, that, as many of the mains were made of Scotch iron, it was thought there was something about the construction of that metal which resisted the effects of electrolytic action.

Another reason was advanced by Professor Sheldon in his paper entitled "Conditions of Electrolytic Corrosion in Brooklyn," read before the American Institute of Electrical Engineers, June 17th, 1900, in which he mentioned his discovery of a thin "silicious compound" of the nature of glass, found upon the surface of pipes, formed there during the process of casting, and attributed that as the "true cause of immunity" as that material was an insulator. In view of the fact of many failures of pipes in Brooklyn since 1899, due to electrolysis, several samples of which we have personally seen (two being shown in this paper, one of the Scotch iron make), it would seem that neither of the above reasons as to *immunity* will stand.

Professor Sheldon also states that this coating is extremely thin and contains perforations.

Such a condition we should consider a good reason for an earlier rupture of a main, than if the corrosion were more evenly distributed over the surface, as at the perforations or spots where there is no coating, the action would naturally localize, and the iron be penetrated more rapidly.

We have noticed in the large majority of electrolytic effects upon cast iron mains, that those spots that are longer one way

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than another, very frequently take a position at right angles to the length of the pipe, as shown in one of the cuts. These lengths of pipe while being handled, are often *rolled* over other lengths or hard surfaces, and this may cause a removal of the coating spoken of at such spots, and the consequent localizing of electrolytic action, which follows the line of the bare iron. This is a suggestion of a further reason that such coating is present, although we can find no comfort as to its presence being a remedy against electrolysis, but rather the reverse. We have recently seen a chart showing the entire surface of a 12-foot, 48-inch main taken from a street in another city, upon which were 80 furrows and pittings, caused by electrolysis. Of the 80 which showed a length as well as breadth, all but 5 (which were quite small) were transverse with the length of the pipe. One was over two feet long and five-sixteenths of an inch at its deepest point. Others were shorter and some deeper, the deepest being nine-sixteenths of an inch.

Our view of the case, therefore, is that electrolysis has been getting in its work upon the Brooklyn mains for several years. If the action has been *slower* than in other cities it may be due to heavier rails or more improved return. The absence, however, of frequent failures of mains from this cause, should not be taken as evidence that electrolysis does not exist; its progress may be slow, slower in some cases than in others. The extent of such progress, however, will not be discovered unless looked for; again, a main may be nearly ruined by this action, but, owing to the pressure of surrounding soil, will hold together and not reveal its state through final bursting for a long time; hence, we believe, there are many places in Brooklyn to-day where this process exists in all its stages, from the small pitting of one-eighth of an inch deep, to those that have penetrated through the mains which are leaking and about to collapse.

In thus reviewing a few instances of the destructive effects of unintentional or uncontrolled currents of electricity, we are conscious that but a comparatively small portion of the ground has been covered, but perhaps sufficient has been shown to emphasize the importance of this evil, referred to in both the first and second parts of this paper. As to considerations for avoiding these effects, any of the able minds in this society are quite competent to suggest solutions, if cases similar to those mentioned should come before them.

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We will, however, give our own view of how some of these effects may be avoided and will briefly refer to each of the points spoken of in their order, trusting that a free expression from others may be had in the discussion.

Earth Currents.—Perhaps the most complete way to avoid earth currents on a telephone or telegraph line when they are so strong as to interfere with its operation, is to adopt the present universal plan and provide a metallic circuit. If this is impracticable on account of the length of line, the case cited will perhaps be as effective as any, *viz.*, seek another "ground." This, however, refers more to private lines in isolated places, rather than central office lines in cities.

Copper-plated Iron Ships.—Should such construction of vessels come to be used, the principal point is to keep the plating intact, free from punctures or abrasions, the hull closely examined when in dry dock, and exposed places upon the iron replated, with a plant which may be carried on board, or kept at the dock; we believe there is merit in the principle of this invention, as the copper and iron form a homogeneous union when properly applied, the same as any case of well applied electroplating.

Propeller Shafts of Steamers.—Although there have been many devices suggested as remedies, the danger still exists in many ships using brass or bronze liners; in some cases they have been done away with altogether. The objection to no bearing, however, would probably be that the shaft itself would be worn, as sand may gain access with the salt water, and when the shaft becomes reduced in size to a danger limit this entire portion would have to be abandoned. It would be difficult even if wise to recommend any one method of several that have from time to time been suggested as improvements, but after a careful consideration of the subject and the known results of using dissimilar metals for such purpose, it would seem the proper thing when seeking improvements to abandon the method of attaching brass or bronze bearings to steel shafts.

Water Meters, etc.—In regard to instruments of this nature used for measuring, or working in liquids, it will be quite apparent that the proper plan is to entirely avoid the use of dissimilar metals in their construction.

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Corrosion upon Bridges.—The case illustrated was mentioned, partly as it is one usually *hid from view,* although above ground, and we think shows the importance of occasional examination at such places; if similar conditions are found upon other bridges, a simple remedy to prevent excessive corrosion at such points would be to keep the iron-work well painted, caulk the seams between the iron and wooden planks with oakum, and pitch or paint the seams over.

Railway Currents.—It is no doubt manifest to those familiar with the situation that the only complete solution for electrolytic corrosion of underground metals by railway currents, is what is commonly known as the double trolley. Such method has been in use for some years in the Borough of Manhattan, N. Y., as represented by the underground conduit system; also in Washington, D. C., where the same system prevails in the city proper, and the overhead double trolley upon some lines in the suburbs, with convenient appliances for changing from one system to the other.

The section of New York we have had under consideration is peculiarly situated geographically—considering also the location of the power house—for the returning currents to take the course we have shown. In our opinion perfect immunity from *possible* electrolytic action upon the subterraneous metals of the two bridges, and *the actual effect* upon portions of the piping system in this section of the city, can only be had either in the method referred to, or a removal of these currents to some other section of the city. Modifications of the present grounded system tending to reduce the straying of railway currents may be undertaken, but changes looking to modifications only, should not be accepted by the authorities as final, or relieving the railway companies in any way from further responsibility in the matter. It is commonly reported that the Kent Avenue Power House with its 12,000 horsepower is to be enlarged to many times its present capacity.

A *third bridge* is to be constructed in the same part of the city we have been considering. The *future* possibilities of damage by electrolysis due to railway currents upon valuable underground structures therefore, as well as those shown to be going on at the present time, should cause grave concern if the electrical conditions, as they at present exist, are to be continued.

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In conclusion, the few instances of corrosion of metals by electrolysis, met with in practice, that time has permitted us to describe are intended simply to illustrate the importance of the subject, with a view to pointing out to those who may be designing or building important works what has already been found in practice, and to suggest methods to avoid the repeating of unfortunate and costly results of others.

One matter of importance, however, we are compelled at least for the present to leave unanswered, and that is whether the metals of a bridge embedded in masonry or concrete can or cannot be affected by electrolysis. We are inclined to believe that in some cases, such as where salt water is present, electrolytic action may prevail to a greater or less extent. The electrical conditions found at the new bridge point to that conclusion, but so far as we know there is an absence of proof on this subject. We cannot examine bridge foundations and cable terminals as we can underground pipes, and for this reason it is a difficult matter to determine. Experiments, however, which are now under way, may in future throw some light on this question, which, we believe, with other questions referred to in this paper, are quite proper to bring before a society of this kind for its consideration.

DISCUSSION.

MR. CARL HERING: Mr. Chairman, I would like to call attention in this connection to some fallacies which exist in the measurement of such currents in pipes and earth currents in general. It seems to me that this is a good opportunity for electrochemists to point out this fallacy. There are two cases: one, in which the current is produced by dissimilar metals, the case first mentioned in Mr. Knudson's paper. The general way to find out whether a current exists is to apply a volt-meter to the two things between which it is thought a current is flowing; if one finds a high voltage it is concluded that there is a large current, while if one finds a low voltage, one thinks there is a small current. But that is is not the case at all. Suppose we take as an illustration a battery, as any two dissimilar metals in moist earth form such a battery. Imagine

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the poles to be connected by some unknown inaccessible conductor, in which we want to know whether a current is flowing. When a volt-meter is applied to those two terminals and there is found a high voltage, it is concluded that there exists a strong current in that conductor; and if there is no voltage, it is concluded that there is no current flowing. As a matter of fact, it is just the reverse; for suppose the conductor has an infinite resistance, then the voltage indicated will be the highest that can exist; yet there is absolutely no current flowing, and no damage being done by electrolysis. On the other hand, suppose the conductor forms a short circuit: the volt-meter will indicate a zero voltage, and it is concluded that there is no electrolysis going on, whereas, as a matter of fact, exactly the contrary is the case as the maximum current is flowing.

The same is true in the other case of a current flowing from an outside source through a pipe. If one wants to know whether there is any current flowing through a pipe or to or from a pipe through the earth, a volt-meter is applied to the two parts between which a current is suspected; if there is a high voltage it is concluded that there is a large current, and vice versa. Here again there exists the same fallacies. Suppose there was a tendency for a current to flow through a pipe, and suppose there was an insulating joint in the pipe; a volt-meter will show a high voltage; but there is no current flowing, as it cannot get through. Take the other case: Suppose there was a very large current flowing, and that the pipe or earth had a very low resistance: the volt-meter will not indicate any volts, and it will be thought that there is no current flowing, while, as a fact, the current is very great. The same is true if the volt-meter is applied between gas and water pipes, or rails, as is usual. Such volt-meter readings are not only no indication, but actually indicate the reverse of the true conditions.

This brings up the subject of how to measure currents flowing in a pipe. We cannot cut the pipe and put an ammeter in circuit. The following method suggested itself to me, although it may not be new. Suppose a pipe with a current flowing through it, and it is desired to know about how great the current is: apply a volt-meter to two convenient points and take the reading, calling it E. Then

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apply an ammeter of as low a resistance as possible between the same points and read the current i, and simultaneously read the volt-meter again; it will read slightly lower,—call it e. With these three readings the current in that pipe can then be calculated. The formula is very simple: the current in the pipe is equal to Ei divided by the difference between the two voltages, that is, by $E-e$.

In connection with the first part of the paper I would like to say that, of course, the corrosion of the iron produced by the copper is according to theory. In other words, iron will rust more readily if in contact with copper than if not; but it seems to have taken people a very long while to learn that this is due to an electrochemical action. If zinc is used instead of copper, the reverse will be true; in other words, if the ships were plated with zinc, then if there is any exposed iron, it will be kept perfectly clean by the electrochemical action of the zinc, as it tends to reduce the iron rust. If, for instance, you want to stop corrosion at the bottom of any iron foundation which is inclined to be wet, a very good and simple way would be simply to electrically connect a block of zinc to that iron foundation, burying the zinc in the ground near-by. The zinc will then act electrochemically in such a way as to keep the iron from being corroded. The zinc will, of course, be consumed in the course of time, but, if attached in the way I suggested, it can be renewed after a number of years. That same method, it seems to me, could be used also to prevent, to some degree, the corrosion of a pipe where it is known that railway currents act to corrode them. We know that the pipe will be corroded when the current leaves it, that is, where the pipe is the anode to the earth. Now, if you electrically connect a wire to that part at that point and secure the other end to a large block of zinc the current in the pipe will tend to become sucked through the zinc by electrochemical action, thus passing out into the ground through the zinc instead of through the surface of the pipe. There is an electromotive force present which will suck the current through the zinc. The zinc will, of course, be consumed and must be replaced from time to time, but this is cheaper than replacing the pipes. It seems to me that it would help to protect the pipe quite appreciably. Not only will zinc prevent corrosion in such cases, but it will also clean

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the pipe. I have made use of that in cleaning some delicate tools which had gotten very rusty. I attached a piece of zinc to them and left them in dilute sulphuric acid for a week or so; on taking them out they were absolutely clean.

DR. N. S. KEITH: I am not up to criticise Mr. Knudson's paper, but I should like to say a word in regard to Mr. Hering's suggestion on the protection of pipe. While no currents are discharging, the zinc would act as a protection to the pipe to which it is connected; but I cannot see how the difference of potential between the zinc and the iron of the pipe, which is a fraction of a volt, will act as much of a protection against whatever currents are flowing through there having an excess of voltage; as, for instance, has been shown by Mr. Knudson, running even up to 25 volts.

I quite agree with Mr. Hering's statement as to the condition of voltage being no guide whatever as to the amount of current and therfore the amount of corrosion, but it is undoubted that these electric railway currents do cause corrosion. If they cause corrosion to the extent to which the difference of potential would seem to point, the pipe would be eaten out in the course of a very short time—perhaps a few days, a few months—much faster than they are; and therefore it would seem the method which Mr. Knudson has set forth of measurement calls for some such arrangement as Mr. Hering has there suggested to determine the amount of current which is flowing through the pipe; but that current which is flowing through the pipe is not the one which causes the corrosion; it is the leakage away from one pipe to some other conductor also buried in the ground.

This question of corrosion of bridges is an exceedingly important one. We have here the big Brooklyn Bridge and another bridge under construction. Their anchorages are held in concrete and granite formations, which are more or less porous to moisture. They are always permeated with moisture. The corrosion which may take place would be an exceedingly slow one, as the mills of the gods grind; but, unfortunately, there must be a corrosion of the anchorages where the currents leave the bridge, either upon the Brooklyn or upon the New York side, as the case might be: and it would seem exceedingly desirable that these anchorages should be investigated, and that most speedily, because we have no

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guide to tell how rapidly such corrosion has taken place. Undoubtedly, theoretically, it has taken place; and the facts should be known about them as speedily as possible.

MR. A. A. KNUDSON: In regard to the method Mr. Hering has referred to, of making tests with the volt-meter—"the high voltage meaning high current and the low voltage meaning low current"—you cannot, it is true, go by that method for current measurements. It does not prove, as he says, that current is actually flowing. Of course, there must be sufficiently low resistance between pipe and rail, or between one pipe and another for current to pass, but the volt-meter gives indications only. It is useful to that extent. Now, in regard to making current measurement upon iron pipes, the first thing is to have the resistance of such pipe. That has been ascertained by an average resistance test of thirty different lengths of cast iron pipe obtained by Mr. D. H. Maury, of Peoria, Ill., and has been worked down to a constant. The constant represents a resistance of one foot per pound of cast iron pipe and that has been used very largely in making current measurements. Comparison readings have often been made, using the direct readings of an ammeter between two ends of pipe, and the results have been found to be very close to those of the fall of potential method. That is the method, therefore, we have used in taking measurements of current readings on cast iron pipe and upon wrought iron pipe as well. The current flow was ascertained in this way upon the pipe referred to in Brooklyn. We went to the extent, however, in order to be as accurate as possible and to prove our test, of procuring a piece of six inch pipe of the same kind, which we measured in Brooklyn and sent to Columbia University. There we passed sufficient current through it until we got our millivolt-meter up to the same maximum reading as we had in Brooklyn; and then we took intermediate and minimum tests, so we think the current readings upon that pipe in Brooklyn are very nearly correct. We don't think they would average 1 ampere in error one way or the other.

The question of placing a piece of zinc upon an iron pipe in a positive district where the current is leaving the pipe—that would act, I have no doubt, in the same way that Mr. Hering has mentioned, but a piece of iron or any other metal would do the same thing. That has already been suggested in a few cases. If I un-

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derstand the proposition correctly, any other metal besides zinc will answer the same purpose.

MR. HERING: Mr. Knudson, it seems, did not understand the function of the zinc. Zinc will act quite differently from a piece of iron; the zinc will act electrochemically to induce the current to leave through the zinc and not leave through the iron, but a piece of iron attached to the pipe has no electrochemical action and could merely act to increase the surface slightly.

MR. KNUDSON: It would act exactly the same way if the zinc was a piece of iron or any other metal. The railway current has to pass out of the pipe in what we call the positive district. If it leaves the pipe itself it must take away some of that metal; if a piece of iron, zinc, or lead is connected with that pipe at such points, the current would probably leave them.

DR. L. BAEKELAND: We all know that iron, in extremely alkaline solution, as well as in nitric acid, has a tendency to become electro-passive, and this fact may have a bearing on the question of corrosion of iron. Solutions of salt, of brine, or solutions which are acid, having even such weak acids as carbonic acid, will have an influence to increase very rapidly the corrosion of iron. Now, would it be possible to prevent this electrolytic corrosion by embedding the iron in a decidedly alkaline medium, for instance, cement, or in any other mixture which would act in liberating or maintaining a decided alkaline reaction? I don't know whether any experiment of that kind has been undertaken; but I think it would be worth while to see if results could be obtained that would prevent corrosion by electrolysis.

MR. HERING: It seems to me that would be rather expensive.

MR. KNUDSON: It would be impracticable on that account.

PRES. RICHARDS: It may be of interest, in connection with Mr. Knudson's remark, that the vessels in the Navy Yard are possibly acted upon by these currents—or were thought to have been acted upon—to know the way in which an aluminum yacht in the Mediterranean came to grief. It was not painted and was tied up to a man-of-war by a steel hawser, and the electric current which passed through the hawser was said, by the newspapers, to have given one of the sailors a decidedly bad shock. The same thing may happen if a copper-bottomed vessel is tied up to a steel vessel

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by means of a metallic hawser. I think it is important that steel vessels should not be tied up in salt water to a vessel which is copper-bottomed.

MR. C. J. REED: I would like to go on record, Mr. President, as doubting the veracity of the man who said he had received a shock from any such galvanic couple. It requires at least six or eight volts to give any very great shock to the human system under the most favorable circumstances and no such electromotive force would be possible from any couple formed of aluminum, iron and salt water.

PRES. RICHARDS: The point I wish to make is that the zinc would protect the pipe. I call to mind the action of zinc used in some steam boilers to protect the boilers. It is a practice which has been in use for a long while, to hang a piece of zinc inside the boiler, in metallic contact with it, in order that the zinc may receive the corrosion instead of the iron of the boiler. It is efficient because the zinc gives up a greater heat energy in being oxidized than the iron. I think Mr. Hering's suggestion of using a block of zinc in connection with heavy iron structures, embedded in the ground, is a very practical one, and would do much to prevent their corrosion.

MR. REED: I would call attention to the fact that at the present time zinc is being used in that way in a great many of our largest steamships to prevent the destruction of condenser tubes. The destruction of condenser tubes has been a very expensive thing in large vessels. It has been found that it can be very materially prevented by inserting pieces of zinc into the condenser in contact with the tubes. The corrosion is a serious matter, notwithstanding the fact that these condenser tubes are made of brass or of copper. The electrolytic effect seems to destroy copper almost as rapidly as brass. Of course, the effect is greatly aggravated by thermo-electromotive forces due to the fact that cold water is on one side of the pipe and hot steam on the other, producing a very great difference of temperature. The only material which seems to have withstood this action any length of time is an alloy made almost entirely of nickel, a patented composition, which is very expensive. I think it costs about $1.00 per pound. This is a very serious question, but it has been found that blocks of zinc placed in the con-

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denser have the effect of materially increasing the life of the tubes.

MR. HERING: I would like to add that theoretically aluminum ought to act still better than zinc, but whether the coating of oxide that forms on the aluminum may not prevent the action from taking place I am not prepared to say.

MR. A. A. BRENEMAN: The common use of pieces of zinc in dyer's kettles (whose organic liquids, faintly acid, are heated) to protect the copper, and, still more remarkable, because representing a much higher intensity of action, the making of tin crystals by dissolving tin in copper kettles in strong, boiling hydrochloric acid, are further examples of this protection of one metal by another. The copper is entirely safe from attack as long as any zinc or tin remains undissolved, simply because of the difference of position of the metals in the electrochemical scale.

There is need of a metal or alloy which, alone, will resist hydrochloric acid, the stronger and hotter the better. Antimony will do this under conditions, but it is not a metal available for sheets or hollow ware.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, President Richards in the Chair.

NOTE ON CORROSION OF ALUMINUM.

By Joseph A. Steinmetz.

The plates shown in the photograph were used in the construction of the Cup Yacht "Defender," and are part of a purchase of scrap aluminum made by the writer's firm about two years ago, when the yacht named was broken up in a shipyard near New York.

The yacht was built of Parsons' manganese bronze, from the water line to the keel, and the free-board plates were of hard rolled nickel-aluminum. I do not know the proportion of nickel, but it was only enough to harden and stiffen the aluminum. The plates were from ¼ to ½ inch thick, averaging ⅜ inch.

From samples which I have preserved (two of which are shown in the photograph) it appears that they were riveted together with steel rivets. Messrs. Herreshoff, the builders of the yacht, disclaim having used steel rivets in connecting the aluminum sheets; but there is no doubt, from the samples shown, that whoever put the aluminum plates in place on the yacht did use steel rivets in contact with those plates.

The yacht was in the water about four years, and showed considerable corrosion at the end of the second year. I am informed that the plates commenced to tarnish and rough-up very soon after being put into service.

Messrs. Herreshoff state that in their opinion the depreciation of the aluminum plates was entirely due to salt water coming in contact with them, combined with the oxidizing influence of the atmosphere. The writer's view is that this action, while certainly taking place, was intensified by the use of steel rivets in contact with the aluminum plates, uniting them to bronze plates, the whole immersed in salt water and subject to conditions of severe atmospheric changes and exceeding humidity.

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The purpose of the communication is to aid in developing the proper field of use and application for aluminum, and to avoid conditions unfavorable to its use.

The excellence of aluminum in resisting corrosion under average conditions of moisture and atmospheric change should not suggest the use of the metal in all combinations or conditions without preliminary experiment and trial.

DISCUSSION.

MR. CARL HERING (communicated): Mr. Steinmetz is no doubt right in saying that the iron rivets intensified the corrosion; they unquestionably would produce an electrochemical action which would make the aluminum the anode and would therefore dissolve it. That the rivets were of steel is shown by the samples, some of which still contain steel rivets. The electrochemical action would also be increased by the manganese bronze, of which part of the hull was made. This would form a true battery with the aluminum part, and as this battery was short-circuited and of low internal resistance the current might have been very great. The electrochemical corrosion might also have been increased by the nickel which was alloyed with the aluminum, if any of the nickel was not combined with the aluminum to form a physical or chemical alloy as distinguished from a mere mechanical mixture of the two metals. If there had been absolutely nothing but aluminum on the outside of the boat I do not believe the corrosion would have been anything like as great; but even in that case if the boat had any iron cranes, like the anchor chain, connected to it, or if it had been secured to an iron pier or with steel ropes, the electrochemical action would have taken place.

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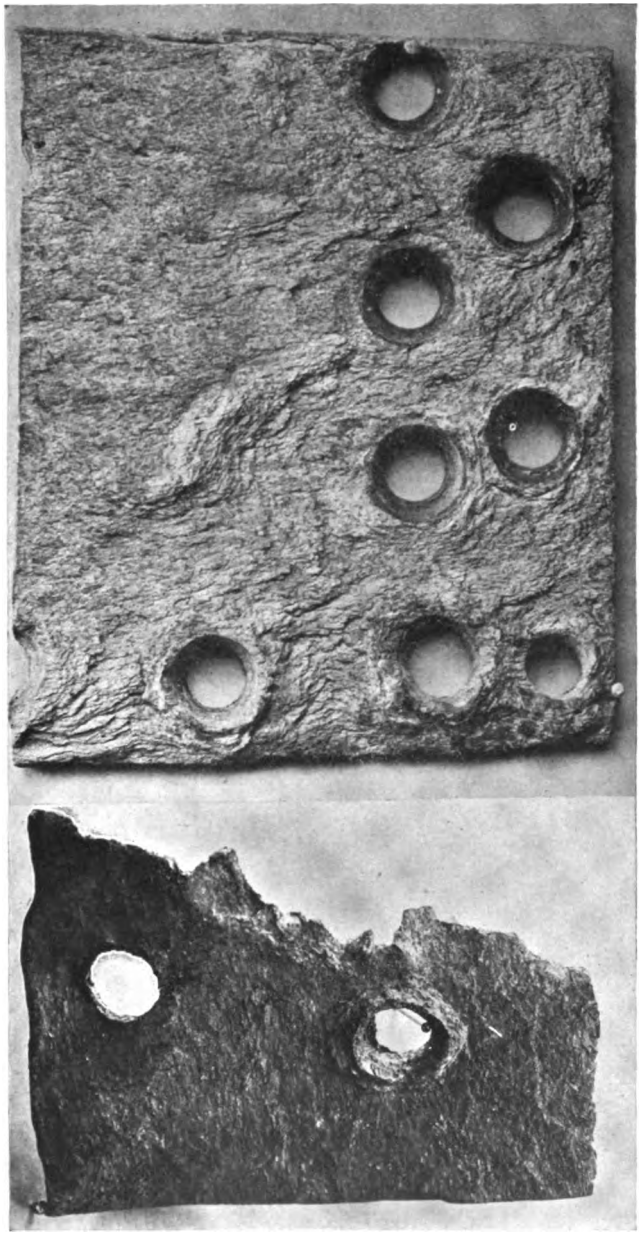

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 16, 1903, Vice-President Bancroft in the Chair.

NOTES ON MODERN ELECTROLYTIC COPPER REFINING.

By Titus Ulke.

Before considering the technical features of this most important branch of electrochemistry, I will call attention to the great difficulty of obtaining absolutely reliable data regarding many electrolytic refining processes and plants. Owing to the peculiar secretive policy adopted by most electrolytic refining companies, admission to their tank rooms is generally denied to visitors of technical training, and in certain large works even to their own chemists. You can picture my surprise when, as chief chemist of the Anaconda Company at its electrolytic refinery in 1892 and 1893, I was not allowed access to the very electrolytic refinery whose solutions and copper material I had to test daily, and whose daily working reports I could freely inspect.

I hold with Dr. Douglas, and have always held, that the managements of copper refining companies might profitably adopt the methods of the American iron and steel makers, and allow engineers access to some or all parts of their plants, and thereby encourage a free exchange of ideas and the obtaining of mutual benefits, which are generally of far greater importance than any temporary advantage gained by secretive methods. There should certainly prevail a greater spirit of brotherhood and sense of fellow ownership in the knowledge of all these subjects and similar secrets gleaned from nature!

As stated by Dr. Douglas in his admirable presidential address to the American Institute of Mining Engineers, there is very little to choose between one brand of electrolytic copper and another. All are good and all have been brought to that high standard by expert labor and expert experiments with instruments in expert establishments, whereas, had there been co-operation on points of purely technical manipulation, the same results would have been obtained at infinitely less expense.

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All the so-called mysteries of electrolytic copper refining may be resolved into certain, now more or less well known, simple rules of practice, which I shall briefly outline in the following pages.

The material at present subjected to profitable electrolytic treatment in the world's copper refineries is invariably a precious metal-bearing crude copper, cast into anodes assaying at least 96 per cent. Cu, with only one or two unimportant exceptions, and generally refined by fire methods up to 98 or 99 per cent.

The initial cathode sheets, or starting plates of plants arranged according to the multiple system, are invariably thin sheets of electrolytic copper, obtained by deposition upon and stripping from greased, oiled or varnished plates of either copper or lead. The commercial cathodes are allowed to reach a thickness which is generally fixed at 0.5 to 0.75 inch in the multiple process, and 0.25 to 0.45 inch in series arrangements.

Solutions containing not less than 12 per cent. and not over 20 per cent. bluestone, and from 4 per cent. to 10 per cent. free sulphuric acid, are employed almost universally. It is very important that the constantly decreasing acidity and the constantly increasing copper contents of the electrolyte be maintained within these limits. A small quantity of common salt or magnesium chloride, or better, hydrochloric acid (say 300 cc. to a tank full of solution), is always added upon commencing operations in order to hinder any possible dissolving of silver and to prevent "sprouting" or brittleness of the cathodes or starting sheets. Ammonium sulphate is sometimes added to the solution when considerable arsenic is present.

Heating the electrolyte up to between 40° and 50° C. is advantageous, because it decreases the electrical resistance of the solution, and increases the tensile strength of the copper. It is essential to maintain the temperature as evenly as possible at the point fixed upon, and to avoid appreciable differences in temperature between the upper and the lower portions of the solution.

Current densities ranging from 4 to 45 amperes per square foot of cathode surface are employed, the amperage used depending chiefly on the cheapness of power, the grade of the anode in silver and impurities, and the purity of the electrolytic solution.

The voltages measure from 0.1 to 0.3 volt between each row of plates in series tanks, and generally from 0.2 to 0.4 volt between

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the tanks when the plates are arranged according to the multiple system, depending chiefly on the current density adopted, composition of the anodes and electrolyte, temperature, structure of the electrodes, and the actual distance between the electrode plates.

The following products of refining are marketed: Commercial cathodes, which are occasionally shipped to the consumer as such, but are generally cast into wire bars, ingots, cakes or slabs, of standard dimensions and weight. They usually assay from 99.86 per cent. to 99.94 per cent. Cu. The yield in commercial cathodes is 97 per cent. to 99 per cent. of the weight of anodes treated, barring the anode scrap, which ranges from 7 per cent. to 15 per cent. of the anode weight in multiple plants, to as much as 30 per cent. (probably) in a certain refinery with electrodes arranged in series circuit. About 1 to 3 per cent. of the copper treated is generally recovered as blue vitriol.

Besides electrolytic copper and bluestone, many refineries produce fine silver and fine gold, together with some base bullion from the anode slimes, and occasionally nickel salts, arsenious acid and tellurium, which products are recovered in purifying or working up the foul electrolytes.

A comparison of the methods and appliances used to-day with those employed only ten years ago, shows that many important improvements have been made, nearly all of which are of American origin, and resulted from the necessity of handling large outputs.

The chief improvements, in my opinion, are as follows: The substitution of casting machines for hand-ladling, resulting in the saving of considerable time and expense; the employment of mechanical conveyors and of pneumatic tongs or hooks for charging pigs into the anode furnaces; charging machines designed for the same purpose; improved anode molds and shape of anodes; the introduction of electrode-handling cranes for charging the entire tank load of plates at one operation; greater facilities for handling material by rail in and out of tank rooms; improved form and construction of solution pumps; improved disposition and operation of tanks, so as to increase their capacity with the same floor space; improved design and support of tanks so as to increase their life and at the same time permit of their ready inspection for leaks and economizing in floor space; arrangement of plant with head room

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below the tanks, so as to allow of a ready removal of the silver slimes from the tanks, and to the silver refinery; improved circulation devices, applicable in special cases; reduction in the size, and consequently in the cost, of tank conductors, excepting the leading-in and leading-out mains; standardization of the conditions in refining, due to a better knowledge of the chemical and physical conditions involved; increase of current densities, so as to increase tonnage and reduce expenses per given output; better checking of the chemical and mechanical properties of the electrolytic copper, so as to enable absolute guarantees to be given with each shipment; simplification of the testing methods in the chemical and physical laboratories, and a general increased efficiency of plant and reduction of operating costs.

As the subjoined tables, taken from my book on "Modern Electrolytic Copper Refining" show in detail, the electrolytic refineries in the world are now producing copper at the enormous rate of 322,295 tons (of 2,000 pounds) annually, and having a value of $96,688,500, with copper quoted at $300 per ton. Over 86 per cent. of this tonnage is furnished by the United States. This country also produces silver and gold, as by-products in electrolytic copper refining, representing a value of over $20,000,000 annually.

The total generator capacity of the world's electrolytic refineries does not much exceed 15,000 kilowatts, or about 20,000 horse-power, of which amount 20 per cent. may be figured as held in reserve, leaving 16,000 horse-power available in depositing copper.

As the world's production of electrolytic copper now averages 883 tons daily, slightly over 18 horse-power are ordinarily required per day of 24 hours per ton of output. The actual cost of producing commercial cathodes from 98 per cent. anodes varies from $3 to $15 per ton.

There are now in active operation or ready to be placed in commission thirty-three electrolytic copper refineries, of which ten are located in the United States, and supply 764 tons daily or 86.5 per cent. of the electrolytic copper production of the world, while six refineries are situated in England and Wales, and furnish a little over 8.8 per cent., nine in Germany, producing about 2.8 per cent., four in France, furnishing a little over 1.6 per cent. of the total ascertainable copper output, the four remaining works being located in Austria-Hungary and Russia.

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ELECTROLYTIC COPPER REFINERIES IN EUROPE.

Country.	No.	Name of company and location of works.	Kind of material chiefly treated.	Approximate daily copper output in tons (2,000 lbs).	Number and capacity of generators. Kw. = kilowatts.	No. of tanks in refinery.	Arrangement of electrodes.
Great Britain.	1	Bolton & Sons, Ltd., Froghall, England.	Gold and silver-bearing "bottoms."	18 to 20 (Cap. 24)	Eight @ 75 Kw.	550	Multiple.
	2	Pembrey Copper Works (Elliott's Metal Co.), Bury Port, South Wales.	Gold and silver-bearing "bottoms."	18 to 20	386 Kw.	1065	Multiple.
	3	Bolton & Sons, Ltd., Widnes, England.	Gold and silver-bearing "bottoms."	10 to 12	Four @ 75 Kw.	240	Multiple.
	4	Leeds Copper Works, Hunslet, Leeds, Eng.	Chili bars (96 per cent. Cu.).	10 to 12 (Capacity)	Four @ 170 Kw.	216	Elmore.
	5	H. H. Vivian & Sons, Swansea, Wales.	Gold and silver-bearing "bottoms."	8 to 10	300 Kw.[1]	.....	Multiple.
	6	M. Kechnie Bros., Widnes, England,	Miscellaneous crude copper.	9	Three @ 75 Kw.	234[1]	Multiple.
Germany.	1	Norddeutsche Affinerie, Hamburg, Germany.	Miscellaneous crude copper.	10	Ten @ 8 Kw.[1]	600	Multiple.[1]
	2	Mansfeld Kupferschieferbauende Gewerkschaft, Eisleben.	Gold and silver-bearing "bottoms."	5	90 Kw.[1]	.....	Multiple.
	3	Communion Huettenwerk, Oker.	.....	5	Sixteen @ 4 Kw.[1]	600[1]	Multiple.
	4	Borchers Bros., Goslar.	.....	1	20 Kw.[1]	.....	Multiple.
	5	Elmore Metall-Actiengesellschaft, Schladern an der Sieg.	Chili bars.	1[1]	20 Kw.[1]	.....	Elmore.
	6	Stadtberger Huette, Niedermarsberg.	Argentiferous cement copper.	0.9 to 1	20 Kw.[1]	.....	Multiple.
	7	Altenau Kupferhuette, Altenau, Harz.	.....	0.8 to 1	One 21 Kw.	.....	Multiple.
	8	C. Schreiber, Burbach, Siegen.	.....	0.2[1]	One 11 Kw.	.....	Multiple.
	9	Allg. Elektro-Metallurgische, Gesellschaft, Papenburg a. d. Ems.	Ni + Cu matte.	0.2[1]	10 Kw.[1]	.....	Hoepfner.
Austria-Hungary.	1	Bergbau u. Eisenhuetten-gewerkschaft, Witkowitz.	Pyrites cinders from acid works.	0.25 to 0.3	Two @ 4 Kw.	72	Multiple.
	2	Berg u. Huettenverwaltung, Brixlegg, Tyrol.	Black copper (90 per cent. Cu.).	0,12 to 0.14	Two @ 5 Kw.	60	Multiple.
France.	1	Société d'Electro-Metallurgie, Dives, France.	Chili bars.	10 to 12	Four @ 170 Kw.	216	Elmore.
	2	Société Anonyme des Fonderies et Laminoirs, Biache St. Vaast.	.....	2[1]	Five @ 6 Kw.[1]	100[1]	Multiple.
	3	Grammont, Affinerie, Pont de Cheruy.	.....	1.1[1]	25 Kw.[1]	....	Multiple.
	4	Hilarion, Roux et Cie, Marseilles.	.....	0.28[1]	One @ 3 Kw.[1]	40	Multiple.
Russia.	1	Kalakent Copper Works (Von Siemens & heirs), Kalakent, Caucasus.	Blister copper.	1.2 to 1.4	Two @ 24 Kw.	102	Multiple.
	2	Nikolajov Works, Nijni Novgorod.	.....	0.75	20 Kw.[1]	70	Multiple.

[1] Doubtful.

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ELECTROLYTIC COPPER REFINERIES IN THE UNITED STATES OPERATED IN 1902.

No.	Name of company and location of works.	Kind of material chiefly treated.	Approximate daily copper output in tons (2,000 lb.)	Number and capacity of generators. Kw.= Kilowatts.	No. of tanks in refinery.	Arrangement of electrodes.	Approximate daily output of gold and silver from slimes.
1	Raritan Copper Works (United Metals Selling Co.), Perth Amboy, N. J.	Converter Copper from Boston and Montana, Butte and Boston, Old Dominion, Arizona Copper, Cobar, Copper King, Ltd., Highland Boy, United Verde, Bingham and Greene Consolidated Co.'s.	150 to 200 (Cap. 200)	Five @ 600 Kw.	1,600	Multiple	8,000 to 10,000 oz. Ag. 175 to 200 oz. Au.
2	Guggenheim Refinery (Perth Amboy Plant) of Amer. S. & R. Co., Perth Amboy, N. J.	Anodes and pig copper from Mexico, Utah, and Colorado.	100 (Cap. 150)	Three @ 520 Kw.	816	Multiple	25,000 oz. Ag. 200 oz. Au.
3	Anaconda Mining Co., Anaconda, Mont.	Anaconda anodes.	84 (Cap. 150)	Three @ 240 Kw. Two @ 360 Kw. Four @ 220 Kw.	1,430	Multiple	9,000 oz. Ag. 40 oz. Au.
4	Nichols Chemical Co., Laurel Hill, N. Y.	Converter copper from the Mountain Copper, United Copper, Copper Queen and Granby Co.'s and metal from the Canadian and Spanish pyrites cinders.	120	Six @ 75[1] Kw.	120	Series	6,000 oz. Ag. 204 oz. Au.
5	Baltimore Smelting & Rolling Co. (Baltimore Copper Works), Baltimore, Md.	Converter copper from anaconda, Mt. Lyell, and part of the Germania Works output.	80 (Cap. 100)	Eleven @ 80 Kw.	540	L. P. series S. P. multi.	6,400 oz. Ag. 28 oz. Au.
6	Boston and Montana Cons. Copper and Silver Mining Co., Great Falls, Mont.	Boston and Montana anodes.	75	Two @ 810 Kw.	324	Multiple	5,000 oz. Ag. 70 oz. Au.
7	Balbach Smelting & Refining Co., Newark, N. J.	Orford anodes and miscellaneous.	45 (Cap. 50)	One @ 300 Kw. Two @ 125 Kw.	430	Multiple	3,000 oz. Ag. 15 oz. Au.
8	De Lamar Copper Refining Works, Carteret, N. J.	Blister copper from Bully Hill mines, Cal., the Tacoma Smelting Co. and U. S. Mining Co.	50	One @ 520 Kw.	428	Multiple	10,000 oz. Ag. 200 oz. Au.
9	Buffalo Smelting Works, Black Rock, N. Y.	Lake Superior argentiferous native copper "mineral."	30	One @ 510 Kw. Two @ 48 Kw.	270 490	Multiple	600 oz. Ag. — oz. Au.
10	Chicago Copper Refining Co., Blue Island, Ill.	By-products and miscellaneous pig copper.	5	Two @ 64 Kw.	250	Multiple	100 oz. Ag. 3 oz. Au.

[1] Doubtful.

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For description of all these works, plans and cost sheets of a typical modern refinery, and for a more detailed discussion of the technical conditions of electrolytic copper refining, I must refer to my book on this subject, an advance copy of which is in the hands of the secretary of this Society.

DISCUSSION.

DR. N. S. KEITH: Mr. President, in the history of scientific investigation it has happened many, many times, that the statement of a single fact has upset the finest theory that has been elaborated, and it will probably continue to be the case. Furthermore, I wish to say a little more on the question of local action which takes place at impure anodes. In electrolytic refining the anodes are impure. There is, combined with them, silver and gold, which in the solutions used are electronegative to the copper; and we know that contact of two different metals having electropositive and electronegative relations produces local action. This local action tends to increase the solvent action of the solution at the anode, and more copper will go into the solution, as has been stated briefly by Mr. Johnson. Therefore, from time to time, the electrolytic refiner is obliged to remove from his solution some copper in the shape of sulphate, or otherwise. Otherwise his solution would increase very much in quantity and would involve an increase in the size of the plant and increase in the number of the anodes which he would have in use.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

NOTES ON THE COMPOSITION OF ELECTROPLATING SOLUTIONS.

By N. S. Keith.

In general terms the title refers to solutions of metals such as are used as mediums for the transfer of one or more of the metals constituting an anode from it to a cathode; but more especially to those wherein it is desirable that the metal removed by solution from the anode shall be substantially equivalent in quantity to the metal deposited on the cathode, thus keeping the medium always of the same composition.

This ideal condition is never fully attained, even by the strict observance by the operator of all of the theoretical, chemical and electrical conditions, owing to various unavoidable circumstances necessitated by such commercial reasons as cost, time, character of product, etc.

In electroplating and electrotyping, the anodes should be of the pure metals; otherwise, if the impurities be metals electropositive to that which is transferred, they will either enter the electrolyte, thus changing its constitution by the introduction of undesirable salts, or they may, if insoluble, form crusts on the anode, consisting of insoluble and non-conductive salts.

For example, from a copper anode containing iron, in a copper sulphate solution, iron will be dissolved and more copper will be deposited on the cathode than is dissolved from the anode; in this way the constitution of the electrolyte is progressively changed until finally it becomes unfit for use.

Again, if there be lead in the anode, a lead sulphate is formed thereon; if in considerable quantity, there may be a partially-insulating coating on the anode, which obstinately adheres thereto or falls off from time to time. *But in this case,* as well, more copper is deposited on the cathode than is dissolved from the anode, finally destroying the integrity of the electrolyte.

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In cases where there are metals which are electronegative to the copper of the anode there is a local electrolytic action by which copper is dissolved beyond the equivalent due to the operative current, and to the deposit on the cathode, so that the electrolyte is unduly enriched.

In the operation of electrolytically refining copper all of these conditions exist; though opposed they seldom, or never, counteract each other, either to prevent or to neutralize the actions. Therefore, the electrolytes in refining have to be more or less frequently regenerated by change in quantity of one or more of their constituents, or discarded altogether for new.

The ideal electrolyte, wherein metal is to be transferred, is a solution of that metal which has no corroding effect on either the anode or cathode when no current is flowing through the cell. Such a solution may possibly be made, but in operation, with current passing, it is maintained with difficulty.

For instance, a neutral cupric sulphate solution has, unaided, no appreciable effect on pure copper. But under the action of current, except of quite low density, coatings of a basic sulphate form on the anode, and, for a time, more copper is deposited than is dissolved. Then, in order to pass current, an increase of voltage is necessary. Then follows a deposition of hydrogen on the cathode with an equivalent oxidation of the anode without corresponding solvent action. A less density of current and agitation of the electrolyte will allow the equivalent of the anion SO_4, and of the cation Cu. It must be observed that if the anion SO_4 be supplemented by O or the cation Cu be supplemented by H from the water of the solution, there is decomposition of the electrolyte. True, there is, in any case, continuous composition and decomposition, as the synthesis and analysis are equal and opposed; but so far as changing the composition of the electrolyte is concerned that may not be considered, if the necessary ions only are moved by the current.

If the cupric sulphate solution be acidified by addition of H_2SO_4 then the current density may be increased, because there is more of the anion available. But it may be necessary to increase the quantity of Cu, so that the quantity of cation may be equal to the extent of fully satisfying the requirements of the density of current. Otherwise H will be deposited with the Cu and the electrolyte depleted of its essential constituent, Cu.

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Agitation of electrolytes is necessary in operating with high densities of current in order to have abundant supplies of the suitable ions at their proper places at the surfaces of the electrodes. Heat assists both agitation and solvent action, but that ceases to be valuable in these cases if the desired action at the cathode cannot thereby be made equivalent with that taking place at the anode.

The foregoing considerations justify the conclusion that the use of strong solutions as electrolytes, with abundant solvent of the salt formed at the anode and rapid agitation or circulation, will allow of great densities of current, insuring rapid deposits of metal. These interdependent conditions, properly balanced and operated, will insure, also, the desired quality of deposit, within the characteristic possibilities of each metal as to its crystallinity or its amorphous condition.

Solutions for electroplating should, in inoperative condition, have little or no action on either anode or cathode. But, however, this is not the case with many which are in daily practical use. Take, for instance, a solution of gold cyanide in a solution of potassic cyanide. This is generally worked while hot.

Now, gold is not, contrary to popular acceptation, dissolved by a solution of potassic cyanide. But auric cyanide is. To dissolve gold in a solution of potassic cyanide without electric current it is necessary to furnish some element to displace the CN of the KCN so that it may be free to unite with Au to form AuCN. This element, in practice of cyaniding gold ores, is oxygen. If only half of the necessary oxygen be supplied there is a further change involving the decomposition of some of the water of the solution, as expressed by this formula:

$$4Au + 8KCN + O_2 + 2H_2O = 4(AuCN.KCN) + 4KOH.$$

It will readily be seen how essential is the presence of oxygen.

By exposure to air such a solution absorbs oxygen and thus becomes a ready solvent of gold, from both electrodes, thus changing the solution. Under current, CN is the anion and acts directly to unite with the gold of the anode. But such a solution is worked with a high voltage and high density of current, for practical results, with a strong evolution of both oxygen and hydrogen.

To preserve the integrity of the electrolyte, in so far as its contents of gold is concerned, the electroplater varies the area of the

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anode, making it more or less, to increase or decrease the contents of gold so dissolved; generally by guess, under the "rule of thumb," guided by experience. The cathode is kept in constant, rapid motion to remove the bubbles of hydrogen, so that the gold cation may have access to the cathode surface.

Such coatings of gold have quite imperfect adhesion, especially on metals which are electropositive to gold in cyanide solutions. To obviate this defect, as much as possible, the operator makes the necessary electrical connections to the electrodes before immersing the cathode in the bath.

Gold is seldom deposited to any thickness exceeding one-ten-thousandth of an inch, and oftener not more than one-hundred-thousandth of an inch. Such a deposit cannot be considered a protective coating for a great length of time, even under ordinary atmospheric conditions, and not at all under the action of corrosives of the metallic body which it overlies.

No matter how well the article may have been cleaned[1] or how well it may have alloyed with the gold,[2] or been bombarded,[3] the deposit is porous and the metal underneath is still subject, though in a lessened degree, to the action of corrosive gases and liquids. The oxides, chlorides, nitrates and sulphides thus formed at the exposed places on the baser metal require more room; so they exude, creep under the coating, and spread themselves over it, so as to, in time, completely hide the gilding. Thus it may be mistakenly thought to have found its way, as an alloy, into the substance of the baser metal. Etching will dissolve the oxides, etc., and again expose the gold on the surface of the article.[4]

No matter how nearly perfect an electroplating solution may be, nor how skilfully operated, the deposit increases in roughness with thickness. In electrosilvering the operator from time to time removes the cathode and smooths the deposit by "scratch-brushing" with a brush made of metallic wires. He is thus enabled to secure any desirable thickness of deposit of silver, and a thoroughly protective coating, because he closes the pores of the deposit by the burnishing action of the brush.

Those solutions, used in the transfer of metals, which contain

[1] Burgess and Hambuechen: Electrochemical Industry, 1, 204.
[2] Kahlenberg: Electrochemical Industry, 1, 201.
[3] Johnson: *Ibid.*, 1, 212.
[4] Kahlenberg: Electrochemical Industry, 1, 201.

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no free acid of the kind which is a constituent of the salt of the metal transferred, are the most permanent and least liable to decomposition in operation, provided that salt is readily soluble in the liquid, and that liquid has no action, by itself, on the metal.

For example, some years ago the author began a series of experiments, having for their object the refining of lead base-bullion, and separating its contents of gold and silver by electrolysis. His first work was done in solutions of lead acetate and of lead nitrate.[1] But the integrity of such solutions could not be maintained. They were gradually decomposed with the formation of basic salts insoluble on both anode and cathode, and some soluble in the liquid. The deposits then became unsatisfactory.

Such solutions in the cases of all metals are impracticable for continuous work on a large scale. Like effects are the result in working cyanide solutions if the cyanogen constituent is not, from time to time, renewed.

I overcame this defect in the process of refining lead by using as a vehicle for the transfer, lead sulphate; and as a roadway a solution of sodic acetate, in which lead sulphate is readily soluble.[2]

The anion SO_4 readily attacked the lead anode, and the solution of sodium acetate at once dissolved the lead sulphate.

In this solution, without access of oxygen, lead remains bright and unattacked. Under the action of current of reasonable density its integrity is preserved indefinitely. The same amount of lead is deposited as is dissolved, and no gases are evolved. The acetate of soda remains unchanged.

The general tendency in electroplating solutions in operation is to form oxy-salts at the anode. Or, in other words, oxygen becomes an active anion to act jointly with the acid anion of the salt which is the true vehicle by which the transfer is made.

This is undesirable, and if avoided, either by suitably composing the solution, or by properly operating it, the best results will be attained.

[1] U. S. Patent No. 209,056, October 15, 1878.
[2] U. S. Patent No. 215,463, May 20, 1879.

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DISCUSSION.

PRES. RICHARDS: Perhaps Mr. Heath has some remarks to make on the regularity of metallic deposits as affected by the nature of the current used; I refer particularly to the use of unipolar dynamo currents.

MR. H. E. HEATH: With regard to that, I do not know that I have anything in particular to say. Dr. Keith's paper was very interesting, and I quite agree with it in every particular. Of course it is a subject that could be talked on all day—perhaps two or three days, to go into details; but he covered it generally, and all I can say is that I thoroughly agree with him in what he says.

With regard to unipolar apparatus, of course it has been known ever since Faraday's time that a machine of that kind could be built, and I had the pleasure of designing such a machine that has been in operation for about eight years. In fact, about a couple of months ago they sent up for new brushes, the first they have needed. The principle is simple enough, the only advance in this particular case being the use of a rotating cylinder, or armature of iron, and in that way cut down the reluctance of the magnetic circuit to such a point as to make the machine commercially practical. It has the advantage of giving us a current that is of the same character as one obtained from a battery; in other words, without pulsations of any kind. From this we get at least two advantageous results. We are able to carry a higher current density for a given reguline quality of deposit and we are also able to vary the nature of the solution and obtain a satisfactory deposit. We find that the pulsating current from a commutating machine requires a solution closely proportioned as to its constituents, in order to get a satisfactory deposit, whereas, with a unipolar machine you are able to vary these proportions considerably. For instance, with copper sulphate and acid you are able to get practically similar deposits with dense sulphate and almost no acid, or with a weak sulphate solution, and considerable acid and with any intermediate strength.

MR. C. O. MAILLOUX: I was very much interested in Dr. Keith's paper, one reason being that I had the honor and privilege of being associated with him nearly twenty years ago in some of his earlier metallurgical work. Dr. Keith is, as perhaps many of you know, the pioneer electro-metallurgist in this country; and I was

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pleased to have him make reference to his lead-refining process, which, it seems to me, is well worthy of being put on record as a very ineresting process, theoretically, which had the misfortune of being too far ahead of its time. I saw with pleasure, in a recent number of *Science Abstracts,* that a comparison was made between that process and the Tommasi process—another process of lead reduction—in which it is stated that the Keith process would be more practical industrially. I was very much pleased to see that, because it is a recognition, late though it may be, of a really interesting scientific process. The one great feature of theoretical interest in this case is the fact that the real electrolyte, sulphate of lead, is not itself primarily soluble, but that we have to depend upon a solvent to keep it in solution.

I well remember at the time that we were engaged in working the process experimentally, the frequent discussions which we had with scientific men, as to the impossibility of producing electrolysis with an insoluble electrolyte—sulphate of lead being recognized as an insoluble substance in nearly all solutions, it was denied, in the light of the then existing knowledge, that it could serve usefully as an electrolyte; and we were repeatedly asked to find some other explanation for the phenomena of electrolysis which took place in the practical working of this process. The reaction, however, was undeniable; the results were certainly precise and in exact accordance with the results which might be expected from theoretical considerations, on the assumption that sulphate of lead did act as the electrolyte.

Dr. Keith's paper also makes an interesting reference to the effect of hydrogen; that is, the tendency to deposit hydrogen. This is another one of the phenomena of electrolysis which at first had the misfortune of being denied and of receiving only very late recognition. I remember having occasion to mention that fact at a meeting of scientific men some twelve or fifteen years ago; and the idea that the hydrogen could be deposited at the same time as copper was simply laughed at.

When I asserted that soft copper deposits were due to the tendency to deposit hydrogen, owing to insufficient quantity of the cation in the solution, the idea was pooh-poohed as preposterous. We now recognize this as a valid principle; and it is

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only right to state that Dr. Keith was one of the first men to foresee and to recognize that principle. The constitution of the solution, as we now know, has a great deal to do with the permissible maximum current density that is consistent with a good reguline deposit. I had occasion, nearly eighteen years ago, to conduct some experiments with a view of developing an industrial process of quick electrotyping, which gave me an opportunity to note the effect of the solution in a very striking manner. At that time electrotyping was a "trade," not an art, very much the same as it is now, the ignorance of electrotypers being, perhaps, a little more dense than it is now. I hope the Electrochemical Society will, by its publications, and by the good work it is doing, infuse some spirit of ambition into electrotypers as a class and lead them to study, so that they may arrive at some higher stage of development than that which they occupy when they think that the weather has something to do with the quality of the deposit. (Laughter.) At that time it was denied by electrotypers that it was possible to obtain good electrotype copper "shells" when the current density exceeded that which a certain machine, of which they did not know the voltage or current output, would produce. The proper way of measuring the thickness of an electrotype was to determine when it was thick enough so that it could be properly "backed" with lead to make a good printing plate. That thickness, I find, was somewhere between 0.005 and 0.015 inch. The time that was then required was somewhere about four or five hours, to obtain a thickness of 0.005 to 0.006 inch; and it was considered that the number of pin holes in a plate and the rate of deposit were very much influenced by the weather and other particular "hoodoo" conditions existing in the particular establishment. To make a long story short, having seen that the largest allowable current density at that time was somewhere between 20 and 30 amperes, I determined to see how far it was possible to push the current density and still obtain a first-rate reguline deposit. I also determined to ascertain how far it was possible to eliminate the so-called "hoodoo" conditions. I am pleased to state that the results which I obtained were obtained by purely theoretical means. They were the result of scientific investigation rather than practical application. In other words, I

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first solved the problem in the laboratory; I then found no difficulty whatever in doing it industrially. I succeeded in getting splendid copper in 1885, with current densities of 500 amperes per square foot, and in reducing the time required to produce an electrotype plate of a given thickness from six hours to less than three-fourths of an hour. I may also state that, previously, the proportion of plates showing "pin holes" or defects was something like 10 per cent, on an average, though it would rise to as much as 50 per cent. on certain days and under certain conditions, which were ascribed to atmospheric and other "hoodoo" influences. I succeeded in raising the efficiency of the plant to such a state that we could get 98 per cent. perfect plates on an average.

Now you may be interested in knowing how this was done. It was done by the very simplest means. I first made a careful study of the specific resistance of copper solutions by a method which I devised for that purpose. I imported from France a "Breguet" outfit—a Wheatstone bridge with telephone, made for the special purpose of measuring electrolytic solutions. By a special cell, the cubical contents of which were known, I was enabled to determine the specific resistance and temperature of the solution. I then made experiments to determine the resistance of various solutions in terms of temperature, acidity and amount of copper sulphate contained therein. I satisfied myself that if I would get good copper, I must furnish copper ions in the solution in such manner that the current could have them and appropriate them at a sufficient rate to furnish the deposited copper; because if the solution does not furnish the cation, copper, fast enough the current will deposit hydrogen; and I found that the best results were obtained by a certain degree of relatively great acidity, with as much sulphate of copper in the solution as the solution would hold and as high a temperature as could be used practically. The next point was to agitate the solution thoroughly, and I used air. The point made by Dr. Keith is very well taken indeed. The effect of air as an oxidizing effect at the anode is not to be neglected. It has something to do with quickening the electrochemical effect. The solution was maintained at a temperature which was just the limiting temperature at which it would not affect the wax used in the electrotyping moulds (or matrices). That temperature was somewhere between 110° and 120° F. I do not have in mind at the

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present time the figures as to the density of solutions; but I want to state one interesting fact, which was that I automatically maintained the temperature of the solution by adjusting the distance between the electrodes at just the proper distance, such that the I^2R loss, or the heat produced by the current passing through the solution would keep the temperature at the proper limit. In that way I got an automatic heat effect and was enabled to regulate the heat in solution to just the proper degree of temperature. This would vary slightly between winter and summer; but the difference was very slight, and it was practically negligible from day to day, *i. e.*, the diurnal variation was negligible. I still have two plates representing the page of a newspaper which I electrotyped at that time by that process; each of them was deposited with a current density of not less than 500 amperes per square foot—possibly a little more. The means of measurement that we had at that time were somewhat crude, and I could get exactly the current density only by calculation from the total weight of copper deposited, in a given time, on a given surface, and from the well-known electrochemical constants. I assure you that the copper obtained under those conditions is very fine and ductile, and has all the mechanical properties which copper had previously had when depositing at rates of from 20 to 30 amperes per square foot.

In conclusion I want to call attention to another interesting fact which has some relevancy to this question, namely: that it has been found in electrolytic refining plants that there is a certain maximum current density consistent with the most economical results. It is possible to construct a curve of the cost as a function of the current density, and it is found that that curve has a minimum point. There is a certain current density which gives the lowest operating cost. Now, strange to say, that current density is rather low. Theoretically (since we can get very good copper deposits at 200, or 300, or 400 amperes per square foot) one might expect that one could raise the current density in electrolytic refining plants to a very much higher figure; but, strangely enough, we find that that figure is not over 50 amperes per square foot, and in many cases it falls under. There are others here who have had more experience than I with electrolytic refining plants and it would be interesting to have them state their opinion on that subject.

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MR. A. H. EDDY: There are one or two things in connection with what Mr. Mailloux has said regarding the density of the electrotyper's knowledge, which I came in contact with many years ago; that was, that he seemed to be impressed with the fact that if he had been getting good work out of the solution which he was using, when he came to change his machine, if he did not get the same results that he did before, the fault must be with the machine. To demonstrate that that was not so, I made the following experiments, which were intended to prove the question, and apply perhaps more intelligently to his case. I showed him that he could make a good shell from almost any condition of solution. I began, if I remember rightly, with 8° Baumé (the scale they were in the habit of using) of copper sulphate and 1° of acid, and then gradually increased that to 8° of acid; I then took 9° of sulphate and corresponding quantities of acid, and in that way I made 240 shells, all of them appearing to be equally good. That is, the current density was regulated so as to give a perfect deposit in each case. That was to show him that he could get good copper provided he adjusted his voltage or current density to his particular solution; but what I wished to do to show him further was that by changing his solution he could get perhaps more rapid results than he was getting. I found it very difficult at that time to induce them to change their solutions from what they had been using. I also found, in making these changes, that it was advisable to keep somewhere near the range which he had been using; because they were very loath to make any radical changes in the way of solutions, and I found that there was a point between the extremes which gave me a much less resistance than was to be found at either end; and we adopted a solution in that neighborhood as a practical one for him to get the most rapid shells, with the conditions that he was willing to work under.

MR. REED: I would ask Mr. Mailloux what part in the chemical reaction the oxygen, which he says was blown into the sulphate at the anode, had in producing the final effect. As I understand the electrochemical reaction, we have at every stage

$$Cu + CuSO_4 = CuSO_4 + Cu,$$

and I do not see where any oxygen can enter the equation. Will you please tell me where to put the oxygen in that equation?

MR. MAILLOUX: I never gave much thought to the theory of it

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except to consider that oxygen ions might neutralize hydrogen ions whenever the current density is high. I do not think it has much influence at low current densities, but at high densities there is a tendency to deposit hydrogen at the cathode and a corresponding tendency to the evolution of oxygen at the anode, and where the solution is agitated there is probably some effect by means of which the two tendencies neutralize. Sometimes energy is required in oxidizing certain impurities, and some of these impurities of the copper have an electrochemical relation to the copper itself, and there is a secondary chemical reaction which takes place there, in which the oxygen can serve a useful purpose.

While I am up I want to supplement the interesting remarks of the gentleman who preceded me by testifying further to the inertia of the electroplater. I found, myself, great indisposition to depart from well-established methods. The "8° Baumé" solution was looked upon by them with holy reverence. I may state that my process suffered from it. I completed my experiments and put the process on a perfect industrial working basis and left it in that shape in charge of a young man who conducted the simple chemical testing operations necessary to maintain the solution in a proper working condition. When this young man left, the electrotypers were disinclined to either find another competent man or to try to learn themselves; and they went back to the old process, even though the other was so very much superior. There were plenty of men who knew the old process with 8° Baumé unheated solutions, not agitated, and as that process was supposed to work more or less without any attention, they went back to it.

MR. REED: It seems to me that the queston I asked is not answered at all. I do not know of any theory by which the introduction of oxygen or air into a solution is going to neutralize hydrogen ions.

MR. MAILLOUX: I do not either.

MR. REED: I do not see how we can introduce any mechanical energy into an electrochemical reaction. The result was, I think, produced mechanically, by stirring the solution, and causing the mechanical transportation of material; I think the same result would have been obtained practically if a stream of any other gas, such as nitrogen or hydrogen, had been used.

MR. MAILLOUX: I did not try that.

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MR. REED: Unless it can be shown that the oxygen has some function as oxygen, it seems to me that that conclusion is unwarranted.

MR. MAILLOUX: One of the points which had escaped me is that it tends to change cuprous into cupric copper and that to some extent may account for the phenomena. In fact, I was not able to differentiate the effect of different gases because I did not have a current of carbonic acid, nitrogen, nor any of the other gases; but it always seemed to me the effect was greater than could be accounted for on any theory of circulation alone. I have tried circulation of another kind, merely pumping the liquid to a height and then circulating the liquid itself; and I find under those conditions I do not get as good results. The solution required more attention. I had to add either copper or acid more often and also to purify it more often in order to keep it in proper and uniform condition.

MR. REED: If that theory is correct then there is continuous addition of copper to the solution. In other words, there would be twice as much copper going into the solution as going out, because it would imply that the electrochemical action at the anode formed cuprous sulphate instead of cupric sulphate.

If it is true that cuprous sulphate forms electrolytically instead of cupric sulphate, and if injected oxygen serves to convert this cuprous into cupric sulphate, we have no evidence of that fact. But we have very strong evidence to the contrary. If this were true, two atoms of copper would go into solution at the anode for every atom deposited at the cathode. This would require the removal of four and a half tons of crystals of copper sulphate and the introduction of one and a half tons of H_2SO_4 for every ton of copper deposited at the cathode—a conclusion absurdly at variance with all experience.

MR. EDDY: I also tried agitation by air, but I was unable to detect any difference provided I made my mechanical agitation equal to what I had with air. Then I came to the same conclusion as Mr . Reed, that it was purely a question of sufficient agitation in either case.

MR. W. MCA. JOHNSON: There are two reactions that can occur, namely:

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$$2Cu + \overline{\overline{S}}\,O_4 = \overset{++}{Cu_2} \,|\, \overline{\overline{SO_4}}$$

and

$$Cu + \overline{\overline{S}}\,O_4 = \overset{++}{Cu} \,|\, SO_4.$$

The first one is the formation of cuprous sulphate occurring at low current densities, and the second is the formation of cupric sulphate occurring at high current densities. The cuprous sulphate is oxidized by the air and the copper is deposited from the bivalent cation at the cathode. In the ordinary electrolysis of copper the first reaction proceeds simultaneously with the second. Consequently more copper is electro-dissolved than is electro-deposited. The electrolyte thus grows richer in copper. All electrolytic copper refineries keep this copper content to a constant figure by taking out copper with insoluble anode, or by adding free acid, as is well known.

MR. CARL HERING: It seems to me that this whole question of current density and nature of the deposit resolves itself into this: In the layer of liquid next to the cathode the solution becomes exhausted of its copper, assuming the solution to be copper sulphate; this layer may have a mere molecular thickness, but nevertheless it is sufficient to prevent the copper sulphate from coming into actual contact with the cathode, as the cathode will be connected completely with a layer of something else which contains no copper, or too little to correspond to the requirements of the current, hence the deposit becomes poor; but if the solution be kept agitated very rapidly so as to always keep destroying this layer of exhausted solution next to the cathode then there will always be enough copper in the solution, which is in molecular contact with the cathode, and there will then be more probability of getting a good deposit. This was very forcibly brought out in some experiments made in England some years ago in which the agitation was carried to a very exaggerated extent; the liquid was pumped through a pipe passing through the anode and squirted with great velocity against the cathode, so that the agitation was extremely rapid and it was then found possible to get beautiful deposits of copper with current densities that might be termed enormous.

MR. EDDY: I would like to supplement my last remarks. When I was commenting about the agitation I was merely taking into consideration the old current densities and not refining; but when

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it came to refining with the higher densities, I will say that we did have to remove some sulphate, a small per cent.

MR. REED: It seems to me that this excess of copper sulphate must be that which always forms when sheets of copper are suspended in a solution containing free sulphuric acid. If you blow air through a solution of sulphuric acid in which copper sheets are suspended it forms copper sulphate rapidly. Sulphate formed in this way would, of course, be in excess and would require removal. In the ordinary electrolytic refining plant there is always a large surface of copper exposed in that way to a solution containing free acid and free oxygen. This continually forms copper sulphate, and would do so if there were no electric current at all. I think the necessary removal of excessive sulphate comes from this action which has nothing to do with the electrochemical action. According to the statements made here I understand that the contention is that oxygen blown through a solution at the anode facilitates the electrochemical action, but I see no evidence in any of the facts stated in support of this view. The small excess of copper sulphate which is formed and removed is entirely inadequate to correspond with the theory of Mr. Johnson, that the electrochemical action forms cuprous sulphate and that the air subsequently changes it to cupric.

According to the statement of Mr. Johnson, cupric sulphate forms with high current density, which reaction would not produce an excess of sulphate by the action of atmospheric oxygen. Mr. Eddy says on the contrary that with low current density (which, according to Mr. Johnson, produces cuprous salt and an excess of copper sulphate) he got no excess of sulphate, but with high current density (which, according to Mr. Johnson, produces cupric salt and no excess of sulphate) Mr. Eddy got an excess of sulphate.

With these contradictory statements before us, it would seem that we have no evidence of anything but confusion as to the function of injected air. The small quantity of excess sulphate formed in refining shows that the electrochemical action is not the formation of cuprous salt subsequently oxidized by the atmospheric oxygen, as Mr. Johnson has conjectured. It also shows that such a function of injected oxygen, if it existed, would not be useful, but harmful, since the oxygen would not in that way act as a depolari-

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zer, but would merely accumulate enormous quantities of blue-stone.

MR. MAILLOUX: Why may it not be that the oxygen acts as a depolarizer at the cathode? My own experiments were at high temperatures, high solution densities, and high current densities, and under those conditions I did not find very much excess of sulphate of copper, strange to say, though I always got a reguline deposit; I always ascribed it as due to the fact that I was not depositing any hydrogen, and that I was getting the full electrochemical equivalent in copper. May it not be that the oxygen has the function of acting just like a depolarizer in an ordinary battery, in that way making way for the current to expend its whole energy—electrodepositing effect—by depositing only copper as a cation?

MR. REED: I understand that the oxygen was supplied at the anode, not at the cathode. If the oxygen were supplied at the cathode, Mr. Johnson's theory of oxidizing cuprous sulphate at the anode by the oxygen would be unintelligible. Mr. Mailloux's statement was that the oxidizing effect of the air at the anode is not to be neglected as it quickens the electrochemical effect.

MR. MAILLOUX: I did not wish to be understood as saying that I supplied it at the anode. I simply put air in the solution between the two plates. I intended to say distinctly that I had no theory to offer as to what became of it or how it operated. I have no definite theory as to the way it acted. I simply noticed the fact that it seemed to me in the presence of air used as an agitator, the results were a little bit better.

MR. REED: I understood the statement to be that the introduction of oxygen facilitated the dissolving of copper at the anode. We are now to understand that the introduction of oxygen acts as a depolarizer at the cathode, which means that it takes some of the current which would otherwise be used in depositing either hydrogen or copper. I am unable to see of what use a depolarizer at the cathode would be which would merely absorb current.

MR. C. O. MAILLOUX (Communicated after adjournment): I found one of the note-books containing some of the data concerning the electrolyte, which was used by me in 1885 and 1886, when depositing copper with current densities of 500 amperes per square foot, as stated in the discussion.

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The electrolyte consists of copper sulphate dissolved in water, a certain percentage of free sulphuric acid being added.

The temperature was maintained at about 110° F. It sometimes fell as low as 100° or rose as high as 120° F.

The percentage of free acid (which was always determined by volumetric analysis) was maintained between 4.3 per cent. and 4.8 per cent. It was not allowed to fall as low as 4 per cent. or to exceed 5 per cent., this range having been found to give the best results.

The amount of copper sulphate in solution was such as was required, with a temperature of about 110° F. and about 4.5 per cent. free acid, to give a specific gravity of not less than 23° Baumé, nor more than 28° Bé.

In one instance, it is noted that at 106° F. and 25.3° Bé., and with 4.45 per cent. free acid, the deposit was "very satisfactory."

The notes contain records of densities as high as 30° Bé., but they do not contain any comment on the quality of the deposit.

The electrical resistance of the electrolyte was measured several times a day, and the measured value was always noted with the data relating to acidity, specific gravity, etc.

The regular records of these measurements have not been preserved. Only a few records of such measurements are contained in these notes.

Unfortunately, I have not been able to find the constant by which the measured value was multiplied in order to give the specific resistance, in ohms per centimeter-cube. Hence, the few measured values given in the notes have only a qualitative and comparative value.

According to the best of my recollection, the minimum resistance was not found at the particular density and acidity at which the solution was worked, but at higher degrees of density and acidity. The further increase of temperature would also, of course, further reduce the resistance.

For the benefit of the members interested in the literature of copper electro-deposition, and as interesting illustrations of the early or pioneer contributions of Dr. N. S. Keith to the technology of electro-metallurgy, I would call attention to certain articles published by him in 1877 and 1878, in the *Engineering and Mining Journal*. Dr. Keith's paper on "Copper by Electricity" was read

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before the American Institute of Mining Engineers in October, 1887, and published in the *Engineering and Mining Journal* in December of the same year.

Among the interesting articles published by Dr. Keith in the same periodical may be mentioned a reference to the recovery of copper from waste solutions, and also a serial article on the "Refining of Copper."

An article on "Some Experiments and Deductions in Electrometallurgy of Lead," published July 27, 1878, will be found of special interest, being very far in advance of electrolytic science as it was understood and "preached" in those days.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

ELECTRODEPOSITION ON ROTATING CATHODES.

By J. G. Zimmerman.

In the deposition of metals, both in the plating and refining operations, we are limited, by the physical character of the deposited metal, to the use of a current density of comparatively low value. The rotation of the cathode has been suggested as a means for using higher current densities, and it is the purpose to present herein some data and observations obtained from an investigation of such means recently carried on in the Laboratory of Applied Electrochemistry at the University of Wisconsin. The work here described is only preliminary to a more extensive investigation of the subject which it is hoped will be carried out in the future.

The method employed consisted in the rotation of the cathode, a brass tube 7/8 inch in diameter, attached directly to the shaft of a small electric motor, and in varying the speed, the current density and the composition and temperature of the electrolyte.

The work of others along this line seems to have been confined mostly to copper. Mr. Cowper-Coles has descibed the manufacture of copper tubes by this process and has given some interesting data in regard to this process.[1] I have endeavored to determine whether the influence of rotation which is so marked in the case of copper, is equally effective with other metals, among which are nickel, zinc and silver.

Copper.—In depositing copper it is found that the rotation of the cathode enables the current density to be run up to a high value and at such high values, the physical character of the deposit depends to a great extent upon the speed of rotation. With a comparatively low speed of 700 revolutions per minute, and a current density of 200 amperes per square foot, the character of the deposit is at first very good. After a thickness of about 0.04 inch has been reached the cathode assumes a rough, pebbly appearance, the roughness increasing rapidly as the plating proceeds until

[1] Jour. of Inst. of Elec. Eng., Vol. XXIX, 1900.

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finally some of the higher elevations grow out in the form of trees which point in the direction opposite to that of the rotation. (Fig. 1.)

The fineness of the grain is dependent upon the current density, other things being equal, and the fineness increases with the current density until, at a critical value, a powdery deposit will occur. The increase in the number of revolutions per minute increases the critical current density, although, whether it is exactly proportional, I have not been able to determine. The highest speed which I used was 2,500 revolutions, corresponding to 573 feet per minute, and my observations tend to confirm the statement of Mr. Cowper-Coles that if a peripheral velocity of about 1,000 feet per minute and a current density of about 200 amperes per square foot be used, the copper will plate out with a high polish and to any thickness desired.

Fig. 2 illustrates the deposition at a current density of 160 amperes per square foot, and Fig. 3 at 320. Equal weights were deposited out in each case and other conditions were the same. These samples show that the copper in the second case has finer grain than in the former, although the difference in grain is not sufficient to show clearly in the photograph. The speed was 1,600 revolutions per minute (367 feet per minute) and the electrolyte, as in all the experiments with copper, was a nearly saturated solution of copper sulphate with 10 per cent. of free sulphuric acid. The solution was maintained at room temperature.

Nickel.—Nickel under ordinary conditions of deposition is more sensitive to the effect of variations of the electrolyte and current density than is copper. A very slight change is sufficient to cause a marked difference in the character of the deposit. These effects are equally marked when a rotation cathode is used. Preliminary tests with the single nickel sulphate and other nickel salts failed to give satisfactory results and the ordinary nickel-plating solution, the double sulphate of nickel and ammonia, was then employed. It was found that on depositing from a neutral solution through a wide range of current density upon a polished cathode rotating above 1,000 revolutions per minute and at room temperature, the deposit was of a dull white, similar to that obtained in ordinary plating (Fig. 6).

During the operation, for a short time, and with a high current density, the solution heated about 8° C. and from the fact that the

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FIG. 1.

FIG. 2.

FIG. 3.

FIG. 11.

FIG. 5.

FIG. 4.

FIG. 14.

FIG. 8.

FIG. 6.

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nickel would not corrode from the stationary anode as rapidly as it was deposited upon the rotating cathode, the solution became slightly acidified. Under these conditions the deposit had a polish equal to the best that can be obtained by means of a buffing wheel, and the dull white appearance was entirely absent (Fig 5). This polished appearance was always obtained after operating the plating solution for some time, provided that it was not kept neutral, and it seemed to be due to a change in the electrolyte, resulting from the incomplete corrosion of the anode. To illustrate the dependence of the character of the deposit upon the length of time the solution had been operating, as well as on the current density, five deposits were made which are illustrated in Figs. 6, 8, 9, 10.

The neutral solution was first electrolyzed at a current density of 66 amperes and a velocity of 1,400 revolutions per minute. The first deposit appeared as a dull white coating, as in Fig. 6. The temperature rose from 22° to 26° and the solution then was slightly acid. The second deposit was made under the same conditions as at first, with the exception of these changes in the electrolyte, and the deposit then appeared with a high polish, though with a considerable number of specks on the surface (Fig. 9). On again depositing a coating with 44 amperes density, at the same speed, the deposit assumed its original, dull, white appearance, showing the effect of low current densities on the polish. The temperature was 30° at the beginning and 40° at the end. During an hour's run the temperature gradually rose to 80° and the current density increased from 170 amperes per square foot to 300 amperes. A thick deposit of good quality was obtained. This did not show any indications of cracking or peeling. It was, however, dotted with specks or imperfections, although smaller in size and number than in the previous case. 165 grams of nickel per square foot were deposited in an hour and the indications were that the deposit could have proceeded much longer without becoming loose (Fig. 10). Finally the solution at 80°, after the addition of new salts, was used with a current density of 225 amperes. This resulted in an almost immediate loosening and peeling of the deposited nickel (Fig. 8).

The deposit in all these preceding cases had been discontinued as soon as the loosening or cracking of the coating occurred. A trial was now made to determine the effect of continuing the de-

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posit beyond that point. A hot acid and dilute electrolyte was used; current density 145 amperes per square foot and the rate of rotation 1,000 revolutions per minute. As a result of this lower current density the deposit assumed some considerable thickness before any indications of cracking appeared. When portions of the deposited metal became loose and curled away from the surface, they protected the spaces directly back of them from friction with the electrolyte and in consequence that part of the cathode received a dark powdery deposit similar to the familiar "burned" appearance of nickel. On the other hand, the surfaces exposed to the friction of the solution were highly polished and the unusual appearance of nickel trees on the extreme edges was shown (Figs. 11 and 12).

An interesting phenomenon in the study of nickel is the obtaining of a perfectly polished surface, under suitable conditions. Just what these conditions are I have not been able to definitely determine. It appeared, at first, that it might be due to the solution becoming acidified by the incomplete corrosion of the anode, but the addition of an equivalent amount of free acid to the ordinary plating solution did not seem to afford conditions whereby the same coating could be obtained. The effect of the addition of the free acid was to immediately damage the nickel coating, producing in its stead a brown powder (Fig. 4). That the acidity does effect the deposit materially is shown in Figs. 13 and 14. Both deposits of 17 grams each were made under similar conditions, with the one exception that the second was kept neutral during the whole time. Both electrolytes became hot and dilute in salts, and still the first was highly polished, while the second was of a dull white. The acidity of the above electrolyte far exceeded that which caused the previously mentioned brown deposit. There seems, therefore, to be some other explanation needed than is afforded by the presence of free acid.

All of the nickel deposits obtained, with but one exception, as before mentioned, showed evidences of cracking or peeling sooner or later when any considerable thickness was obtained, and in general, it was found that the greater the acidity, dilution and temperature of the electrolyte the greater was the tendency of the deposit to break up. Fig. 7 illustrates the appearance of such a deposit.

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FIG. 7.

FIG. 9.

FIG. 10.

FIG. 12.

FIG. 13.

FIG. 19.

FIG. 15.

FIG. 16.

FIG. 17.

FIG. 18.

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Zinc.—The behavior of zinc is widely different from that of nickel when deposited on the rotating electrode. While it is difficult to obtain trees or rough deposits of nickel, it is difficult to prevent them in the case of zinc. There is a strong tendency also for zinc sponge to be deposited. While copper and nickel can be deposited in a state of high polish, zinc cannot be obtained smooth unless special precautions are employed. The smoothest deposit was obtained by increasing the friction of the solution against the metal, through the aid of a partition in the cell which prevented the electrolyte from taking up a circulatory motion to correspond with the cathode. The partition consisted of a wooden slab placed vertically in the electrolyte with the edge near the cathode. Figs. 16, 17, 18 and 19 show the influence of such a device. The depositions were obtained from a sulphate of zinc-plating solution and all the coatings were made under equal conditions of current density, temperature and amount of deposit. Fig. 16 shows the results with no partition, the plating being in the form of high, narrow ridges. The result of using the partition at a distance of about ½ inch is to decrease the size and number of the ridges as shown in Fig. 17. By moving the partition to a distance of ¼ inch the deposit is considerably smoother than before (Fig. 18); and by placing the partition very close, but not touching the cathode, a very smooth deposit was obtained (Fig. 19). This phenomenon points to the fact that by employing a much higher speed of rotation, a smooth deposit might be obtained without the partition, but conditions prevented the use of sufficiently high velocities to demonstrate this.

It was found that with an acid solution at almost any current density or a neutral solution at high current density of 225 or over, spongy deposits are obtained (Fig. 15).

Iron was more satisfactorily deposited by this device than by ordinary methods; lead was deposited from a plumbate solution as a thin film with a high polish which, however, flakes off as soon as any considerable thickness is attained and from acetate solutions it was deposited in a spongy form; antimony from a tartrate solution, precipitated to a considerable thickness and with a high polish. This deposit, however, on exposure to the atmosphere for a few days, crumbled to dust. Silver was also plated with great

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rapidity and high polish upon the rotating cathode from a cyanide solution.

LABORATORY OF APPLIED ELECTROCHEMISTRY,
UNIVERSITY OF WISCONSIN.

DISCUSSION.

PROF. C. F. BURGESS: Mr. Chairman, as a discussion of this paper, I should like to point out a few of the interesting features. These experiments seem to show a practical possibility for improvement in the nickel-plating process; for example, a very smooth deposit of nickel may be obtained which requires no subsequent buffing or polishing process. Further, by using 300 amperes per square foot, instead of 6, as is common practice, a suitable coating of nickel may be obtained in one or two minutes, as compared with one-half to three-quarters of an hour, commonly found necessary. To attain these advantages, of course, requires the cathode to be of a shape adapted to the high speed of rotation. Another point which seems to me of interest in this work is that it settles the question which has been discussed in some technical papers, as to what causes the smoothness of the deposit. In a discussion of the Cowper-Coles process before the Institution of Electrical Engineers, it was claimed that it was the centrifugal action throwing away particles of impurities which may be in the electrolyte. Objections were raised to this claim, that in addition to the renewal of the electrolyte caused by the circulation, the smoothness was caused by purely frictional effect. These experiments seem to show that there is a decided frictional action, and that it is not the centrifugal effect which aids in the obtaining of a smooth deposit. This has been shown, for example, by the use of the partition in the cell which prevented the solution from taking up a rotary motion. By preventing the solution from circulating, the frictional effect between the cathode and the solution is increased and thereby increases the perfection of the deposit. Whether the partition is near the cathode or far away from it, the amount of centrifugal action at the surface of the cathode is the same, inasmuch as the speed is kept constant.

MR. CARL HERING: I have been very much interested in this paper, partly because it confirms the very point I raised in the dis-

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cussion of several of the other papers, namely, that it points out the importance of bringing more of the liquid into molecular contact with the cathode. I think that instead of revolving the electrodes, precisely the same effect would have been produced if the liquid had been moved past the cathode with the same speed. It might have been taken out at the one side and forced in at the other. Moreover, I think in practice it would be much simpler mechanically to circulate the liquid by pumping than to rotate the electrodes, especially as they are often of such a shape that they cannot conveniently be rotated. It has also the advantage that it has a similar advantageous effect on the anodes as well; the author stated that in his case the anodes will not take care of such high current densities. I think the explanations given in the paper why the deposit is so much better are not the correct ones. I think the correct explanation is that with high current densities the molecular layer of liquid next to and in molecular contact with the cathode is exhausted of its metal before fresh liquid can get there, hence hydrogen or other things will be set free, spoiling the deposit; or the metal will be deposited only where a few undecomposed molecules are left, thus producing trees or growths. Naturally, if you destroy that molecular layer by either revolving the cathode or by squirting the liquid in between the plates, you will always have the cathode in contact with liquid containing metal.

MR. C. J. REED: I agree entirely with that view, that neither the rotation nor the friction have anything to do with the smoothness of the deposit. It is simply the supplying of the ions of the copper in sufficient quantities to transmit the total current. As the current is increased the rate at which the ions must be supplied has to increase proportionately. Otherwise there is not sufficient copper to transmit the current, and water, the only other electrolyte available, will be decomposed and produce hydrogen. It is the deficiency of the copper and deposition of hydrogen that causes roughness. I do not think that the friction of the liquid has anything to do with it. That can be shown by trying to polish a rough casting of copper by squirting a liquid against it at a high velocity. That would never produce the effect of polishing it. The other point is well taken, that there must be circulation at the anodes as well as at the cathodes. I am not convinced that it is

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mechanically easier to circulate the liquid by rotating the cathode at a higher rate of speed than it is to keep the liquid in motion by other means.

MR. A. H. EDDY: In this same line, a question which came up was how the cathode acts at its surface when the electrolytic film is exhausted. The time taken for that exhaustion, of course, must be very minute. In other words, what should be the speed or movement of electrolytes to equalize the rate of exhaustion? We know that any motion will be of assistance here, but with large currents our electrolyte would have to travel at enormous speeds to produce the desired results. The effect of motion, of course, is to allow the use of higher current densities, but would we not be limited by a maximum rate at which it would be practical to circulate an electrolyte and have it keep ahead of the tendency to form this film?

MR. REED: In other words, the circulation must be speeded proportionally to the increase of current.

MR. EDDY: Yes.

PROF. W. D. BANCROFT: While theoretically it should make no difference whether we rotate the cathode or circulate the electrolyte, practically I think there is a very distinct difference. The important feature is to renew the liquid immediately at the surface of the cathode, and we can do that very well by rotating the cathode. It is very difficult to renew that as frequently by stirring the electrolyte. We have been making some experiments on the deposition of copper and we can of course run a higher current density than usual by good stirring of the electrolyte, but we have never been able to stir the electrolyte sufficiently to reach the current densities that can be obtained without any difficulty with a rotating cathode. I think the difference is just this, that it is not the mean velocity that is important, but the velocity at the immediate surface of the cathode.

MR. H. E. HEATH: A case that has occurred to me, which may have a bearing, is that of a concern in Massachusetts, who happened to have a form of cathode that is a sphere; and by using rotation (I have not exactly figured the current density) they are able to get the very beautiful and soft deposit of copper to a thickness of about one-sixteenth of an inch in less than three hours, which shows at least a fairly high rate of deposition. They find

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one oddity, in that on some of their spheres there will be a line of decrease in thickness running spirally around the sphere, terminating at the bottom; and in this depression, which is not sharply defined, they may have not more than one-half the increase in thickness that they have on the rest of the sphere. It always acts in a spiral running downward, and opposite in direction to the rotation. They asked me to explain the reason for this and I told them I would think about it; and I am still thinking. If anybody can help me, I wish they would.

PROF. BURGESS: As I understand it, Mr. Reed holds that there is no frictional effect and that the question is simply one of a renewal of the solution; I cannot agree with him since, at a low current density, the nickel or other metal ions will be supplied rapidly enough to take care of the current with no circulation whatever. The character of the deposit which is obtained, using such low current densities, is influenced by the rotation of the cathode. In one case it may have a highly polished appearance and in the other a dull white one, the former having all the appearance of frictional action, and not explicable on the supposition that in one case you have a deficiency of nickel ions and in the other case a sufficient number to take care of all of the current.

The maximum current density which it is possible to use is limited not only by the rate of revolutions of the cathode, but more definitely by another factor. This one is the heating effect of the current. A current density of 300 amperes per square foot in any aqueous plating solution will cause heating of the solution to a considerable degree and this heat cannot be carried beyond a certain definite amount.

In regard to the use of rotating cathodes for metal analyses, we have used this method in laboratory experiments during the past year and have found that a metal may be thrown out of solution in a very short space of time, and that satisfactory deposits may be obtained from solutions which are very dilute.

MR. HERING: There is another advantage in circulating the liquid instead of rotating the cathode; in the latter case either half the cathode must be above the solution, which is very bad, because it is then exposed to the air; or else, if the whole apparatus is submerged, there would be a small velocity near the shaft and a high velocity at the circumference, whereas by circulating the liquid

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there would be practically the same velocity all over the cathode. Moreover, bearings, belts or stuffing boxes in the electrolyte are objectionable.

PROF. BURGESS: That depends upon the design of your cathode.

MR. EDDY: With regard to this polished appearance, we find that with a solution of nickel running on the acid side (acid solution) we get the polished appearance in a perfectly clear solution; and I have laid more to chemical action there than anything else. I have seen surfaces fully as brilliant as a buffed surface due to that condition, and by simply neutralizing or rendering it alkaline, it disappeared.

MR. W. R. MOTT: I would like to emphasize that point about the burnishing action of the electrolyte moving on the metal surface. Of course, Mr. Zimmerman does not leave out of account that new solution is continually brought in by the agitation of the electrolyte.

Mr. Zimmerman showed me some of his solutions where copper sulphate was used with a slowly rotating cathode. The copper plated out in tree form and would short-circuit the cell in a few seconds. The short-circuit was interrupted by the breaking off of the tree by the rotation of the cathode. When the cathode rotated faster, trees did not form. This marked change in the physical character of the deposited metal might, by analogy, explain some of the other interesting results.

MR. W. T. TAGGART: Prof. Edgar F. Smith read a paper at the March meeting of the Washington Section of the American Chemical Society in which he gave results obtained in the quantitative determination of metals by electrolyzing salt solutions, using a rotating *anode*. This paper was also read before the Philadelphia Section of the American Chemical Society and a demonstration was given. One-half gram each of mercury, copper, silver, cadmium, zinc, nickel, cobalt and iron was precipitated in 7, 8, 10, 15, 17, 20 and 35 minutes respectively. The anode made from 600 to 800 revolutions per minute; the precipitation was complete and the deposit adherent. With but few exceptions 5 amperes were used; the voltage varied from 4 to 17.

MR. REED: What was the purpose of using such a high electromotive force?

MR. TAGGART: In order to get a high amperage and thereby decrease the time necessary for precipitation.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, President Richards in the Chair.

NOTES ON THE ELECTRO-DEPOSITION OF NICKEL.

BY WOOLSEY MC.A. JOHNSON.

So little definite information has been published on this subject that I felt constrained to make a few remarks regarding this in the February issue of the *Electrochemical Industry*. I think it necessary to add to this by the present paper, which may be considered supplementary and explanatory of the above-mentioned article.

For some time I was employed as electro-metallurgist by the Orford Copper Company, which is the largest nickel refiner in the world. In this capacity and later I made numerous experiments in the electro-deposition of nickel, and studied developments made by other men. Some *theoretical* deductions from this experience will be found below.

The use of hot solution (above 40° C.) has been much praised in the technical press, and has been given, in my opinion, undue prominence. In the first place, the statement that it is impossible to deposit thick coherent coatings at a low temperature is untrue. Perhaps the best piece of electrolytic nickel ever seen by me was a chance deposit on the wire suspending a plater's basket. The solution was cold, but the fortuitous use of a low current density and the great care taken to keep a clear solution caused this remarkable deposit, which was as hard as steel, perfectly reguline, and possessed a dull silver finish. A hot solution has its advantages and its disadvantages, but it is not a *sine qua non* in nickel electro-deposition. In the second place, a hot solution would be used in any electrolytic nickel refining process, not for the reason that thick platings can only be made from a hot solution, but because the voltage can best be reduced by heating the solution as high as possible without causing undue evaporation and consequent creeping of nickel salts. The cost of power in an electrolytic nickel process would be a very large percentage of the total cost, as from five to ten times as much power would be used in

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refining nickel as in refining copper. This is because of the self-evident fact that nickel must be deposited from an alkaline or neutral or very slightly acid electrolyte because of its high electro-positive character, while copper can be deposited from a strongly acid solution, because it is 0.567 volt lower in the electrolytic series. Again, if any working current density were used, say 15 to 30 amperes per square foot, to cut down the interest charge on metal tied up in the vats, the electrolyte would warm up by the $C^2 R$ loss in the vats. In fact, if a cold electrolyte were desirable, which it is not, for the commercial reasons above stated, it would be necessary to place refrigerating pipes in the storage vats to keep the temperature of the electrolyte below 40° C.

There is an advantage in the use of hot solution, namely, to be allowed the use of a high current density and to facilitate circulation. The advantage of hot solutions in making tough deposits has been known to practical electro-platers in this country for some fifteen years. There are several secret "dopes" which can be used to make a smooth homogeneous deposit. I have experimented with fifteen or twenty of these, and it is really surprising to note the benefit that arises from the addition of a very small amount, say one part in a thousand. The excellence of the Balbach nickel cathodes was partly due to the use of a hot solution, which of course was unavoidable, but more to the use of an efficient secret "dope" which was discovered by Mr. William Thum, the present superintendent of the electrolytic plant of the Balbach Smelting and Refining Company of Newark. Mr. Thum is one of the most experienced electro-metallurgists in this country, as with his father, Mr. F. A. Thum, he has worked out practical processes for the refining of copper, nickel, silver, lead, and other metals. The use of a hot electrolyte, which is unavoidable for the commercial and practical reasons above stated, is bad in that it accelerates the reaction velocity of the basic iron, cobalt and nickel salts in the electrolyte. This means that the electrolyte becomes turbid, and a turbid electrolyte always means warty, poor deposits.

Having given a few facts correcting misconceptions regarding the temperature of a nickel electrolyte, I will consider, along the same lines of reasoning given in my previous article on this subject, why the use of a hot electrolyte prevents the cupling-up of

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nickel deposited at high current density. This fact is to my mind directly connected with the formation of nickel-hydrogen alloys.

The capacity of many metals to occlude gaseous hydrogen or "nascent" electrolytic hydrogen has been known for years. This absorption profoundly modifies their magnetic, physical, and electrochemical properties. These effects have been studied by Graham and Troost, Raoult, Hughes, and others. Nickel made by reducing the oxide briquetted with some form of carbon is porous and will absorb 165 volumes of electrolytic hydrogen when placed as a cathode. It will slowly lose this when the current is turned off, and will rapidly lose it when heated in a vacuum. Iron and cobalt have similar properties. A specimen of meteoric ferro-nickel gave up 2.85 volumes of a gas mostly hydrogen which it absorbed in its flight while passing through some hydrogen atmosphere, which of course could not have been very dense.

This nickel hydride is always formed, as is shown by the decreased current efficiency even when no hydrogen is visibly evolved. Another bit of electrolytic evidence shows this. It will be found that nickel electrolysis is not a reversible process like copper refining. A certain amount of work must be done to dissolve the alloys of nickel in the anode, and a certain amount of work must be done to precipitate nickel hydride at the cathode. The instantaneous polarization is quite high and can even amount to 0.50 volt. The continuous polarization is under certain conditions as high as 0.250 volt and measures the electro-positiveness of electrolytic nickel over cast nickel.

Accordingly it is seen that electrolytic nickel, or, to be exact, nickel hydride, is deposited under a considerable electrochemical stress. The molecules of the nickel hydride are in a state of abnormal strain—something similar to the strain of the molecules in tempered steel. This can be proved physically by the following evidence. Nickel was electro-deposited on a malleable nickel cathode sheet, 18x12 inches, which fitted in a groove in the end vat, which was 12¼ inches wide. The groove was made of slats, ½x½ inch in cross section, nailed to the vat. The surface exposed was about 18x11⅛ inches. At the end of six days' deposit out of a hot solution, the electrolytic sheet, still adhering to the soft sheet, was wedged in so strongly that two men were required to pull it out. The whole sheet was now elastic. In addition to

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the potential energy of electrolytic solution tension, as measured by the potentiometer, there was also the potential energy of an elastic body under strain.

Now this elasticity and "over-voltage" (which is really electrolytic elasticity) both gradually decrease with time or with increase of temperature. Electrolytic nickel which is as hard as steel, and brittle, becomes as soft as lead on annealing. This "over-voltage" decreases with time and heat also. Both these properties seem to be dependent on the amount of hydrogen co-deposited.

Take a piece of stiff paper and wet one side of it, allow it to stand and it will be observed that it curls up. Allow it to stand still longer and it will slowly unroll. What has happened? The surface wetted becomes soft as annealed electrolytic nickel becomes soft. The other side is elastic as electrolytic nickel is elastic. Unequal strains are set up and the sheet curls up. When the annealing action of the water soaking through the sheet makes the whole sheet limp, these strains are equalized and the sheet uncurls.

Precisely the same thing happens in the electro-deposition of nickel. The "curling up" of electrolytic nickel is caused by the fact that there is an unequal strain between the inside and outside layer. The inside layer, when deposited, had the same abnormal strain, but with time this tension has become more normal by a slow annealing action of the nickel hydride. The outside layer has had, however, no time for the molecules to adjust themselves, and consequently the tension is greater on the outside than on the inside. The curling is always such that the outside layer (or last deposited) is on the concave side of the bending.

It has been observed that nickel will curl when the temperature of the electrolyte is 60° C. if the current density is too high or if the deposit is made on a heavily oiled or graphitized surface. This layer could not have been uniform, and consequently there were parts of a surface where nickel was thin, causing lines of weakness where the nickel cracked and curled off. The higher the current density, or, better still, the "electrode-voltage," to use the scientific term, the greater the strain. Nickel will often stick to a clean surface, when it will curl up in a few hours from the same surface when oiled. Nickel will stick to a matte or rough surface when it will curl up from the same surface smooth. If the proper

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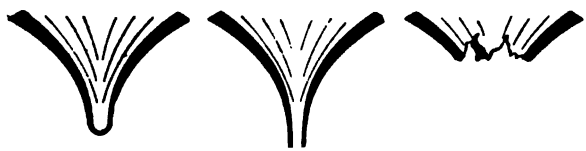
"dope" be added to the solution, nickel has a remarkable hardness and toughness. Mr. Thum took one of his cathodes ⅛ of an inch thick, placed it against a strong wood frame, and fired at this point blank with a Winchester rifle. The bullet was stopped by the nickel cathode and drew out a long cone at the end of which was found what was left of the bullet—nothing. I append a sketch and a description by Mr. William Thum.

If the electrolyte be made gas-free by allowing to drip through a vacuum and be kept in a substantially gas-free condition, it will be found that the tendency to curl up of nickel deposited from this electrolyte is diminished. A large part of the hydrogen which is ordinarily occluded by the nickel, is dissolved by the electrolyte, because the electrolyte has its hydrogen pressure reduced to a low limit. As a consequence, hydrogen is always passing from a state of the nickel hydride to the state of hydrogen dissolved in the electrolyte. It is simply due to the fact that the hydrogen pressure of one is lower than the pressure of the other, and matter always flows from high pressure to low pressure. By this means it is possible to make heavy platings of nickel, provided the circulation of the gas-free electrolyte keeps pace with the formation of hydrogen at the nickel cathode. This process and apparatus for it have been patented by me. The tenacity and reguline character of nickel deposited from a gas-free electrolyte are greatly benefited by this, and for certain purposes, such as the manufacture of "starting sheets" this device would be of value. For general refining purposes it has, in my opinion, small worth.

In conclusion it may be said, as has been said by me before, that the subject of electro-deposition and this special field of the formation of hydrogen alloys at the cathode are as inviting as any in electrochemistry for the research student.

Annexed cut shows in the first figure the effect of firing on the nickel plate referred to. The second figure shows the effect of a



higher power bullet on the same plate; the exit hole was smaller than the calibre of the bullet. The third figure shows the effect of a similar bullet on an eigth-inch thick iron boiler plate.

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DISCUSSION.

PROF. C. F. BURGESS: Mr. Chairman, this paper appeals to me as a valuable contribution from the practical point of view, showing, as it does, how it is possible to overcome one of the most perplexing difficulties that those who have been dealing with the electrodeposition of nickel have encountered. I should also like to lay emphasis upon another feature which Mr. Johnson points out; that is, the necessity of having in the electrolyte no insoluble particles in suspension. The presence of such particles has a greater influence on the physical character of the deposit than is commonly supposed. In fact, it is frequently as important to have the electrolyte clear as it is to have it of suitable chemical composition, in order that a smooth deposit may be obtained.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

NOTE ON ELECTRICAL ENDOSMOSE.

By Wilder D. Bancroft.

Electrical endosmose, or cataphoresis, is a subject which is overlooked in the recent books on physical chemistry and electrochemistry, in spite of the fact that the carrying of the solution through a diaphragm is a disturbing factor which has to be kept in mind in every experiment involving a diaphragm and which may be of great importance in certain cases. In the Hargreaves and Bird process for making caustic and bleach, the cathode chamber is practically done away with, the wire gauze cathode being placed against the diaphragm and the caustic formed at the electrode being washed off by a current of steam and carbonic acid. The success of the process depends in part on preventing any chloride coming through the diaphragm. If the electrical endosmose exceeds a certain value, this will be impossible. One ampere-hour will decompose a little over 2 grams of salt. If we have a solution containing 200 grams of salt per liter or 2 grams per 10 cubic centimeters, an amount of electrical endosmose greater than 10 cubic centimeters per ampere-hour will inevitably carry undecomposed chloride through the diaphragm. In actual practice, a lesser degree of endosmose would probably have the same result. Such a state of things is not impossible. With a 10 per cent. copper sulphate solution and an ordinary porous cup, there is no difficulty in getting a flow of 20 cc. per ampere-hour. As a matter of fact, however, the endosmose of a salt solution, 200 grams per liter, through an ordinary porous cup is small, not over 2 to 3 cc. per ampere-hour. In spite of this, one cannot place a porous cup containing this salt solution in a beaker containing caustic soda solution and electrolyze without further precautions. If one does, one always finds chloride in the cathode chamber. By placing a platinum spiral in the bottom of the porous cup, dipping the porous cup just below the surface of the solution, and placing the

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cathode directly under the cup, I had an arrangement like a plane diaphragm with lines of flow passing through practically the whole surface. With this apparatus no chloride could be found in the cathode chamber after a forty-minute run at an ampere and a half, 2 ampere-hours all told. Keeping everything else the same and sinking the porous cup deep into the solution, a marked amount of chloride was found in the cathode chamber after a twelve-minute run, 0.3 ampere-hour. While it did not seem probable that there could be a reverse endosmose in the upper half of the solution, I have tested this hypothesis by putting sulphuric acid of different concentrations in the anode chamber and copper sulphate in the cathode chamber. In no case was I able to detect any copper in the anode compartment. On the other hand, special experiments showed that a diffusion of the initial sodium chloride solution does not take place to any appreciable extent under the conditions of the experiment. A solution which has been electrolyzed, however, and which smells strongly of chlorine, does diffuse rapidly, and the appearance of chloride in the cathode chamber is apparently due to a diffusion of the decomposition products, or of the solution containing decomposition products at points where the flow of current is relatively small.

While too great an endosmose would be disadvantageous to the Hargreaves and Bird process, it seems possible that a degree of endosmose just insufficient to carry chloride through, might be advantageous. If enough water were carried through the diaphragm, it might be possible to dispense with the steam and the carbonic acid. Since the degree of endosmose varies with the nature of the diaphragm, this is another factor to be considered in the search for the ideal diaphragm.

In certain cases it might be desirable to have a diaphragm which would give negative endosmose, the solution moving in the direction of the negative current. There is, of course, an intimate connection between the behavior of diaphragms and the movement of suspended matter under the influence of the current. In most cases suspended particles move to the anode, which means that the water flows by them in the direction of the cathode. A diaphragm is a porous mass of suspended particles. If free to move it would move toward the anode, provided its constituent particles would so move. If held rigidly, the water moves and moves to the cath-

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ode. With a diaphragm made from particles which tend to move to the cathode, we should have negative endosmose. The experiments of Billitzer[1] in Nernst's laboratory show that it would be possible to make a metallic diaphragm which would give negative endosmose in some solutions. Some preliminary experiments of my own show that the addition of pyrogallol in large quantities, either to copper sulphate or sulphuric acid solutions, has practically no effect on the rate of endosmose through a porous cup.

It is usually believed that electrical endosmose carries the solution through the diaphragm unchanged in composition.[2] While this is usually very nearly true, it can hardly be universally true. In the experiments of Morse[3] on the electrolytic preparation of copper ferrocyanide membranes, he observed a very marked endosmose. If we should take one of these cells before the resistance became enormous and were to place it in a solution containing one electrolyte which could pass the membrane and one which could not, it seems hardly probable that the passage of a current would not cause endosmose with changing concentration. This is, of course, an extreme case, but it should make us careful about assuming that no concentration change can be caused by the introduction of a diaphragm.

[1] Ztschr. Elektrochemie, 8, 638 (1902).
[2] Cf. Lamb: Phil. Mag. [5], 25, 52 (1888).
[3] Am. Chem. J., 26, 80 (1901).

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903. President Richards in the Chair.

IONS AND ELECTRONS.

By Louis A. Parsons.

Soon after Volta's discovery and the consequent construction of galvanic batteries, Nicholson and Carlisle decomposed water into its constituent parts. Sir Humphry Davy with the great battery of the Royal Institution decomposed soda and potash, both of which had been considered as elementary substances. From this work and similar work of other observers, the idea was conceived of the dissociation, or the breaking-down, of molecules of a substance in a liquid state into charged constituent parts. Faraday gave to these charged parts—atoms or groups of atoms—the name of *ions*; those having a positive electrical charge which in electrolysis move toward the kathode, *kations*, and those negatively charged which move toward the anode, *anions*.

If we can conceive that in some way a molecule in a solution is separated into two ions, one charged positively and the other negatively, it is natural to conclude that if two electrodes from a battery are dipped into the solution the positively charged ion will be attracted to the negative electrode and vice versa, and the conduction of electricity through the liquid by means of these ions results. But how are the molecules dissociated in the first place? According to the theory of Grotthus (1805) this dissociation is produced by the electric current. Since a definite amount of energy would be necessary to dissociate a molecule, a minimum electromotive force must exist, below which electrolysis could not take place. When then it was shown that any electromotive force, however small, will cause a current to flow through an electrolyte until the back electromotive force due to polarization stops it, this theory was abandoned. The new theory which Clausius advanced in 1856 assumed that some of the molecules of a substance are dissociated when the substance is dissolved, so that the electromotive force has merely to act as a directive force causing the anions to move to the anode and the kations to the kathode. Evi-

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dently, according to this theory, as these ions are thus removed by the action of the current, more of the molecules in solution must separate into ions, a certain dynamical equilibrium being thus maintained.

As the ions at either electrode give up their charges to the electrode they combine into molecules which may be those of a gas or of an insoluble solid and hence separate from the liquid and may be collected. Faraday found that the ratio of the total mass of the substance formed by electrolysis at one electrode to the total quantity of electricity carried by the ions is a constant for a given substance and is in any case equal to a constant times the chemical equivalent of the element, or what is the same thing, the ratio of the mass of an ion to the charge carried by it is proportional to the chemical equivalent. Hence the charge carried by an ion is proportional to the valence. It has been calculated to be of the order of 10^{-9} electrostatic units[1] (10^{-18} coulombs).

The theory of Clausius was applied by Arrhenius to the explanation of the abnormal osmotic pressure and lowering of the freezing-point in solutions that are good conductors, which according to Van't Hoff's theory of osmotic pressure indicated a greater number of parts present than the molecules of the dissolved substance—such an increase in the number of parts being a consequence of dissociation. From Arrhenius we have the present Theory of Electrolytic Dissociation.

The electrolysis of water (effected by passing a current through water containing some acid) gives positively electrified hydrogen ions which appear at the kathode and negatively electrified oxygen ions which appear at the anode. More than forty years ago Perrot[2] decomposed steam into hydrogen and oxygen by passing an electric spark through it, and found that the decomposition took place not only at the electrodes but also all along the path of discharge, twenty times as much hydrogen being in one case formed as in a water voltameter placed in series. When he collected separately the gases formed at the electrodes he found the same amounts as in electrolysis of water, hydrogen appearing at the kathode and oxygen at the anode. J. J. Thomson[3] repeated

[1] Riecke.

[2] Annales de Chimie et de Physique. (3). 61, 161 (1861).

[3] J. J. Thomson : "Recent Researches in Electricity and Magnetism," p. 181 and appendix.

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this experiment and found that an arc discharge in steam gave the anomalous result of liberating negative hydrogen ions at the kathode and positive oxygen ions at the anode, while the spark discharge gave the normal positive hydrogen and negative oxygen ions. He believed that the spark passing through steam modified that part in the path of the discharge so that the modified ions assumed opposite charges to the normal ones. The arc discharge, being comparatively continuous, passed through the modified gas while the spark following a new path each time passed through the unmodified gas. From this it appeared that the same atom may in the electrolysis of gases be either positive or negative according to conditions.

This work on steam led J. J. Thomson to study the electrolysis of other gases.[1] He sent a current through HCl gas and obtained $\bar{H}$ at the cathode and $\bar{Cl}$ at the anode as was evidenced by the spectra obtained near the two electrodes. By using a mixture of H and Cl in a vacuum tube the hydrogen was transported to the negative electrode and chlorine to the positive. When the vapor of chloroform, $CHCl_3$, was used in the tube, both the hydrogen and chlorine lines were bright near the negative electrode, while the carbon bands appeared at the positive electrode. It appeared that in the series CH_4,CH_3Cl, etc., the chlorine and hydrogen were both positively charged so that in the substitution of Cl for H there is not a substitution of + for — charges. The hydrogen ion Thomson believed might have either a + or — charge, and one experiment seemed to show that the passage of a current through hydrogen gas separated the molecules into $\dot{H}$ and $\bar{H}$ ions. In a vacuum tube he obtained the Hα line brighter than the Hβ near the anode, the reverse holding near the kathode. So far as I know, this experiment has never been repeated.

In the electrolysis of gases at ordinary or moderate pressures the ions seem to be of the same size and to carry the same charges as the ions in the electrolysis of liquids. At very low pressures in a vacuum tube the luminous discharge ceases and the kathode rays are projected from the kathode in straight lines with great velocity, and cause the portion of the tube where they strike to become phosphorescent. These rays are deflected by an electrostatic field and by a magnetic field in just the way in which they would

[1] Nature, 52, 451 (1895).

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if they were negatively charged particles. They are also capable of inducing charges in a cylinder through which they pass.

On the assumption that the kathode rays are negatively charged particles, Thomson experimentally determined their velocity and the ratio of the mass to the charge $\frac{m}{e}$. The velocity he found to vary according to conditions but to be of the order of one-tenth the velocity of light, while the ratio $\frac{m}{e}$ was constant in all cases, and not proportional to the chemical equivalent of the gas contained in the discharge tube.[1] This is remarkable and the more so since e was independently shown to be the same in all cases, which leads to the conclusion that the mass of these carriers is the same for all substances—and not characteristic of the elements as are the masses of the atoms. The value of $\frac{m}{e}$ (when e is expressed in electromagnetic units) Thomson found to be about 10^{-7} while in the case of the hydrogen ion formed in electrolysis $\frac{m}{e} = 10^{-4}$. e is the same for electrolysis and for the kathode rays and is of the order 10^{-19}. This gives for m about one-thousandth the mass of the hydrogen atom.[2] These results of Thomson have been verified by quite a number of other observers.[3]

Thus the kathode rays consist, according to J. J. Thomson, of charged particles, having about one-thousandth of the mass of the hydrogen atom, and are the same no matter what the substance from which they are derived. Thomson has given to them the name of *corpuscles*.[4] Some think that we have here to deal with moving charges not connected with matter, and these charges of negative electricity are called *electrons*[5] or *electrions*.[6]

In a tube giving kathode rays there are also streams of positively charged particles—the so-called canal rays or Goldstein rays—and it has been found by different observers that the mass of these ions is of the same order as the mass of the ions in elec-

[1] J. J. Thomson: Phil. Mag., 44, 293 (1897).
[2] Rapports: "Congrés International Physique Paris," 1900, Vol. III, p. 138.
[3] Seitz: Annalen d. Physik, 8, 238-243 (1902); Townsend: Nature, 68, 413-414 (1902).
[4] Popular Science Monthly, 59, 323 (1901).
[5] Lodge: London Electrician, pp. 313, 348, 385 (1902); pp. 425-732 (1903).
[6] Kelvin: Phil. Mag., 3, 257 (1902).

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trolysis.[1] Thomson says,[2] "The invariability and smallness of the mass of the carriers of negative electricity and the variability and comparatively large mass of the carriers of positive electricity seem to me to point unmistakably to a very definite conception as to the nature of electricity. Do they not obviously suggest that negative electricity consists of the corpuscles, or, to put it another way, that the corpuscles are negative electricity, and that positive electrification consists in the absence of these corpuscles from ordinary atoms?" (Here he has the idea of electrons.) An uncharged atom or molecule is one having connected with it a corpuscle (or enough corpuscles to neutralize it). Ionization consists in the separation of the corpuscle (or corpuscles) from the atom—in gases at low pressure the negative ion is the corpuscle, the positive ion the atom (or group of atoms) which has lost a corpuscle or more. In electrolysis of liquids the corpuscles are attached to otherwise neutral atoms thus charging them negatively and dragging them along through the liquid. Corpuscles in a vacuum tube move so rapidly and consequently possess so much kinetic energy that by their collisions with uncharged atoms or molecules knock off corpuscles and thus ionize the gas. A gas may also be ionized by the passage through it of X-Rays, Becquerel rays, ultra-violet light, by the falling of ultra-violet light on a metal plate in contact with the gas, and by the passage through it of negative ions produced by any cause, if these ions have sufficient kinetic energy. The negative carriers in all these cases have been shown to possess the same mass and to be identical in all respects, as far as can be determined, with the corpuscles in the case of the kathode rays.[3]

The name electron seems now to have been generally adopted to denote one of these free negative charges which are concerned in all electric phenomena. Whether or not these charges actually exist on small particles of matter, as Thomson seems to hold in this theory on the corpuscles, or whether they exist apart from matter—atoms of electricity—we cannot say. The view that the "negative carriers" concerned in kathode rays, Becquerel rays, etc., are not particles of matter but "atoms" of electricity itself, is held

[1] Wien: Wied. Ann., **65**, 440 (1898).

[2] Pop. Sci. Monthly, **59**, 323 (1901).

[3] J. J. Thomson: Phil. Mag., **46**, 528 (1898); **48**, 547 (1899); J. S. Townsend: Nature, **65**, 413-414 (1902); C. T. R. Wilson: Phil. Trans., **192**, 403 (1899).

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by such eminent men as Lord Kelvin and Oliver Lodge. Lodge has lately been publishing an interesting series of articles on electrons in the *London Electrician*.[1] Lord Kelvin suggested the name "electrion"[2] in *Nature* in 1897[3] in which he says "I prefer to consider an atomic theory of electricity, foreseen as worthy of thought by Faraday and Clerk Maxwell, very definitely proposed by Helmholtz in his last lecture to the Royal Institution, and largely accepted by present-day theoretical workers and teachers. Indeed, Faraday's law of electrochemical equivalence seems to necessitate something atomic in electricity, and to justify Johnstone Stoney's word electron. The older and at the present even the more popular name *ion* suggests a convenient modification of it, *electrion*, to denote an atom of resinous electricity." In his paper in the *Philosophical Magazine*, Lord Kelvin makes some assumptions and works out the mathematical consequences which lead one to some rather fanciful ideas as to the arrangement of the electrons in an atom. He assumes that two electrons or two atoms without electrons repel each other according to the inverse square law, and that every atom attracts every electron outside of it with a force also inversely proportional to the square of the distance between the centers; and that electrons can freely pass inside atoms, the force inside varying directly as the distance from the center. "The neutralizing quantum of electrions for any atom or group of atoms has exactly the same quantity of electricity of one kind as the atom or group of atoms has of electricity of the opposite kind. The quantum for a single atom may be two or three or any integral number and need not be the same for all atoms." Two atoms which have the required number of electrons to neutralize them are "uncharged" and exert no force on each other. If there is a deficiency of electrons in the atom it is said to "have a positive charge;" if there is an excess of electrons a "negative charge" results. Differences in the quality of the atoms, according to Kelvin, may be explained by differences in the number of electrons required to neutralize or by differences in the specific force exerted by the atom without electrons.

At the time of the discovery of the kathode rays and of the experiments which seemed to prove that they were charged particles,

[1] Electrician, 50, 313, 348, 385, 425, 732, 863 (1902-3).
[2] Phil. Mag. (VI), 3, 257 (1902).
[3] Nature, May 27, 1897.

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J. J. Thomson published in the *Philosophical Magazine* what Lodge has aptly termed an "epoch-making paper," a mathematical investigation of the effects of a moving electrically-charged sphere.[1] He found that as a result of the motion a magnetic field would be produced, that the moving charge would experience a resistance due to its charge just as if its mass were increased, and would be acted on by electric and magnetic forces, so that streams of electrified particles would behave in the same manner as kathode rays. Theoretical work along this line has been done by Heaviside,[2] Schuster, Lord Kelvin, Abraham[3] and others.

Let us consider such a charged sphere. When the sphere is at rest, removed from all other charges far enough so that they may be considered at infinity, the charge is uniformly distributed over the surface and there exists at each point in the surrounding medium an electrostatic force,—electrostatic lines of force extend radially outward from the charge equally distributed throughout all directions in space. When the charge moves to an adjacent point the whole system of lines of force or stress in the ether is displaced, but this displacement cannot occur at the same instant of time throughout all the surrounding space and without producing some effect in the ether due to its motion. If the charge were annihilated at a given point and immediately recreated in an adjacent point, the stress would not be immediately recreated about the second point out to infinity but would travel outward with the ordinary speed of propagation of stresses or impulses in the ether, *i. e.*, with the velocity of light. As the charge moves forward there is a change in the electrical force at any point fixed in the ether which increases as the charge approaches, reaches a maximum when it is nearest, and again decreases. This variation in the electrostatic stress causes other stresses in the ether which are steady so long as the motion is steady and are along closed circles concentric about the path of motion—the magnetic lines of force. This magnetic field is also carried forward, is a maximum in the equatorial plane and is proportional to the charge and the square of the velocity. If the velocity is not great in comparison with the velocity of light, the magnetic force at any point, P, considering the motion to be along a line, C B, is given by the equation

[1] J. J. Thomson : Phil. Mag., V, 11, 229 (1881).

[2] Oliver Heaviside : Phil. Mag., Apr., (1889), p. 324 ; and Electrical Papers, Vol. II, p. 504.

[3] Max Abraham : Annalen d. Physik., IV., 10, 105 (1903).

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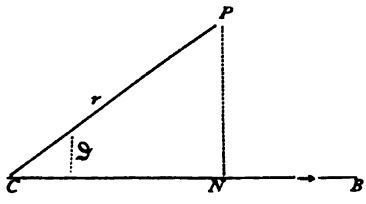
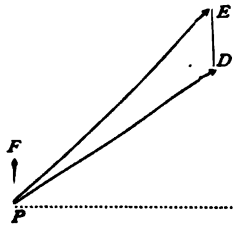


$$H = \frac{e\,u \sin\vartheta}{r^2}.$$

(The charge is at C, $CP = r$, $PCB = \vartheta$, e = the charge and u the velocity), and its direction is *up* from the paper at P. The electric force given by the equation

$$E = \frac{e}{Kr^2},^1$$

is directed radially outward from P; but the motion of the magnetic field through the ether produced, by induction, another electromotive force $\perp$ to both the direction of motion and the magnetic force, *i. e.*, extending upward from P in the direction NP.



If PD be the normal electric force (in direction and amount), and $PF = DE$ the induced electromotive force, the resultant electric force is PE. The effect of the motion is to increase the electric force at a point and to turn it toward the equatorial plane. With increasing velocity the lines of electric force, although remaining radial, move up more and more toward the equatorial plane. The same change in the magnetic force also occurs. In the case where the velocity equals the velocity of light all the force and all the charge are concentrated in the equatorial plane.

As long as the velocity is constant the electric and magnetic fields are steady (if referred to the moving charge as center). Whenever the velocity is increased the magnetic field is increased and this brings in the phenomenon of electromagnetic induction producing an induced electromotive force in such a way, according to Lenz's law, as to oppose the increase in the magnetic field, *i. e.*, along the line of motion and in the sense opposed to it; hence by increasing the velocity a force is brought into play opposing the motion. If the charge is stopped a reaction results tending to keep it in motion. Thus the charge acts as if it had inertia, and the effect of the charge is to increase the inertia and the kinetic energy of the moving sphere. We may speak of this increase of inertia as the "mass" of the charge. For a charge e

[1] K is the specific inductive capacity.

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on a sphere of radius a (in air or ether) the "mass" $= \frac{2e^2}{3a}$[1] (provided the ratio of the velocity to the velocity of light is small). As the charged sphere moves in a region where there are external electric and magnetic forces it will experience a mechanical force tending to deflect it in the direction of the electric force and one tending to move it spirally around the line of direction of the magnetic force (if such force forms an acute angle to the direction of motion). Just such deflections as these have been observed in the case of the kathode rays, and, as has been said, all the phenomena of kathode rays are just such as would be produced by streams of negatively electrically charged spheres. When the kathode rays strike a target they heat it, as would be the case if the target were subjected to a bombardment of material particles.

Whenever there is a sudden change in the velocity there is a sudden change in the distribution of the charge on the sphere. If the sphere moving at great speed is suddenly stopped there results a violent agitation (and oscillation) of the charge on the sphere. Suppose that due to a collision, the agitation is so great as to knock the charge entirely off the sphere and that it moves on through the ether. We can conceive of it as moving with a velocity comparable with the velocity of light, as the kathode rays appear to do. It possesses inertia and will act accordingly. By virtue of this inertia it will have kinetic energy, and mechanical force will be required to stop it. It will be deflected by electric and magnetic fields just as the sphere would be with the charge on it, and since in stopping it must give up its energy we may have a heating of a target even though the charge is not carried by a particle of ordinary matter. Thus we can explain all the phenomena of kathode rays on the assumption that they consist of electrons or negative charges.

If this electron traveling along a vacuum tube strikes against an atom (or molecule) which when neutral we shall assume to contain a given number of electrons and by its collision knock off an electron from the atom, the latter becomes positively charged. These positively charged atoms having greater inertia move more slowly. Such are the canal rays. Thus the electron by collision with the molecules of a gas ionize it. Because of the sudden stoppage

[1] If there is a uniform surface distribution when at rest.

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of the electron when it reaches a solid metal surface, electrons may be thrown off that surface and they in turn ionize that gas. If X-rays, which are generally believed to be pulses of light, *i. e.*, abrupt changes in the electromagnetic stress in the ether, strike upon a neutral atom they may cause such a violent agitation as to knock off an electron or two, *i. e.*, the X-rays will ionize a gas. The same thing we would expect to occur in the case of the very rapid vibrations known as ultra-violet light.

In the case of liquids the electron could not move the great distances that it does in a vacuum tube, and because of the absence of this freedom the electron would not long remain detached from atoms. In the dissociation of the molecules the positive ion consists of an atom or group of atoms without the necessary electrons to render it neutral, while the electrons detached from it attach themselves to the other atom, giving it a negative charge. The passage of the current is effected by the motion of the electron and atom together and by the handing over of the electron from ion to ion. Not only in gases and liquids but in metals as well we are to think of conduction as the transference of electrons. Lodge[1] considers three kinds of conduction (1) the "shot method" which takes place in gases under low pressure, where the electrons are projected comparatively great distances with immense velocity, (2) the "bird-seed" method taking place in electrolytic conduction in liquids where the electron is carried by the atom or group of atoms and then dropped (like the bird carries the seed), and (3) the "fire-bucket" method—the ordinary metallic conduction where the electron is handed along the line from molecule to molecule or atom to atom.

The theory leads us further and assumes that electricity exists only as electrons and any possible electric current is only moving electrons. This being true the Rowland experiment that a moving electric charge is equivalent to an electric current follows of necessity.

Let us return now to our consideration of the motion of a charged sphere—or the spherical electron. To recapitulate, when the electron is stationary it is surrounded by a steady radial and uniformly distributed electrostatic field. When the electron is moving *with constant velocity* it carries along with it an electro-

[1] See paper in the Electrician, December, 1902, Jan., 1903, etc.

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static field which is radial and steady (at points determined by coordinates from axes fixed in the charge) but is the more nearly concentrated in the equatorial plane the more nearly the velocity approaches the velocity of light, and carries along with it a steady magnetic field which is circular and concentric around the line of motion. Whenever the velocity changes there is a reaction opposing the change. But there is something more. Whenever the motion is accelerated there is an increase in the magnetic force and hence an increase in the electrostatic force. This increased stress in the ether starts near the charge and moves with the velocity of light radially outward as electromagnetic radiation through the ether. Radiation occurs whenever an electron is accelerated in its motion and is caused only by the accelerated motion of an electron, for it has been shown that the motion of matter itself cannot set the ether in motion. When a kathode ray electron in a vacuum is suddenly brought to a stop there is a sudden and intense radiation of energy: a single pulse or series of pulses of rapidly decreasing amplitude are sent off through the ether followed by the pulses at irregular intervals as other collisions occur, *i. e.*, Röntgen rays originate at the point where the kathode rays strike.

If there is a regularity in the acceleration of the electrons, a series of waves are sent out. Not only does radiation occur whenever the speed is changed but results from centrifugal acceleration as well. If an electron moves around the common center of gravity of itself and the atom to which it is connected, or if according to a late conception it revolves in an orbit inside the atom, there is a centrifugal acceleration and so long as it thus moves there is an electromagnetic radiation outward of a period equal to the period of revolution of the electron. If this period is great electric waves result, if the period is less we have the Reststrahlen, or if still less, the long heat rays, if comprised within the limits of the visible spectrum, light, if the wave length is still shorter, ultra-violet light. The explanation of the polarization of these waves, the rotation of plane of polarization by a magnetic field, the double refraction of transparent crystals, and total reflection is given by the electromagnetic theory of light.

If a magnetic field is produced perpendicular to the plane of the orbit of the electron its speed will be increased or decreased ac-

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cording to the direction that it happens to be moving in its orbit, and a change in the wave length of the emitted light will result. The theory of electrons revolving in orbits, as developed by Lorentz and others, gives a complete explanation of the Zeeman effect—the production of triplets, etc., in the spectrum from a substance in a magnetic field.

The theory of electrons having free periods of vibration existing in solids furnishes an explanation of metallic reflection, absorption and anomalous dispersion.

The Aurora Borealis has been explained as due to the passage through the rarefied gas of the upper atmosphere of the electrons, perhaps given off by the sun, following the lines of force of the earth's magnetic field (really winding as spirals around the lines).

The Hall effect is due to the deflection by the magnetic field of the electrons from the straight course as they are handed over from atom to atom in the conduction of a current through the metal.

Since the velocity of the electron as it revolves in its orbit in the atom is very great, the centrifugal force may at some time exceed the attractive force, in which case the electron will be shot off from the atom in a straight line with an immense velocity enough to carry it through matter and cause it to ionize gases and other substances by knocking off electrons from the atoms. Electrons may be ejected even though they are not vibrating in orbits so as to produce light. All substances seem to give off electrons spontaneously. Some give them off at a vastly greater rate than others. These are the radioactive substances, and the emission of these electrons constitute the Becquerel rays.

We have seen that the mass of an electron *i. e.*, its inertia, is about 1/1000, the mass of a hydrogen atom, *i. e.*, about 10^{-26} grams. That is, it bears about the same relation to the mass of a gram weight, as that of the gram does to the mass of the earth. From the equation $m = \frac{2e^2}{3a}$, the radius of the electron can be calculated. $a = \frac{e}{m}$. e, e, as given by Riecke's[1] experiments, is between 2.10^{-10} and 2.10^{-9}; $\frac{e}{m}$ from the experiments of Simon[2] and

[1] E. Riecke: Lehrb. d. Phys., 2, 308, 386 (1902).
[2] Wied. Ann., 69, p. 599 (1899).

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Seitz[1] is 1.86×10^{-9} (for the kathode rays). This gives

$$10^{-13} < a < 10^{-12} \text{ cm.}$$

The radius of a hydrogen atom has been calculated to be about 10^{-8} cm. Hence the radius of the electron is about 1/10,000 or 1/100,000 of the radius of an atom, or about the ten millonth or hundred millionth part of a wave length of light. If dimensions were magnified so that a wave length of light would extend from Baltimore to New York, an electron would be about as large as a bullet or marble. Magnified in the same proportion a foot rule would cover the distance from the earth to the sun. If an atom were magnified until it were a globe a hundred feet in diameter, or made as large as the Johns Hopkins Physical Laboratory, an electron would be about the size of the dot on an i on a printed page.

The value of m, the inertia of the electron, given as $\frac{2e^2}{3a}$ holds only in case the ratio of the velocity to the velocity of light is not great. For high velocities the inertia is a function of the velocity, increasing as the velocity increases. This is analogous to the formation of a sheath of compressed air which is carried along by a bullet in its flight thus producing an apparent increase of mass. Abraham[2] in his mathematical investigations of the motion of an electron came to the rather remarkable conclusion that the mass of the ion determined by the ratio of a force applied along the direction of motion to the resulting acceleration is not the same as that determined from a force acting at right angles to the path and tending to deflect it. He distinguished the two as the "longitudinal" and "transverse mass." Both increase with the velocity but the longitudinal mass the more rapidly. Denoting them by m_l and m_t respectively and the ratio of the velocity to the velocity of light by β they may be expressed by the series

$$m_l = \frac{2e^2}{3a}\left(1 + \frac{6}{5}\beta^2 + \frac{9}{7}\beta^4 + \frac{12}{9}\beta^6 + \cdots\right),$$

$$m_t = \frac{2e^2}{3a}\left(1 + \frac{6}{3 \cdot 5}\beta^2 + \frac{9}{5 \cdot 7}\beta^4 + \frac{12}{7 \cdot 9}\beta^6 + \cdots\right).$$

Determinations of the velocity of the more rapidly moving Becquerel rays give values for the mass which increase with in-

[1] Ann. d. Physik., 8, 233 (1902).

[2] Max Abraham : Ann. d. Physik., 10, 105 (1903).

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creasing velocity; and in some recent work Kaufmann has found values of the mass of the Becquerel rays for different velocities which satisfy the second of Abraham's formulas given above.

At the present time it may be said that our ideas in regard to electrons are just beginning to crystallize. We cannot say that this or that is the true explanation, nor do we know that electrons as we have pictured them exist; but certainly the theory is a fruitful one, and it is with interest that the physicist, and I should presume the electrochemist as well, awaits future developments in this line, both theoretical and experimental.

BALTIMORE, MD.

DISCUSSION.

MR. C.J. REED (Communicated): Whatever may be the nature of an electric charge—whether it be an electron, atom of electricity, or an ethereal stress—an electrically charged body, atom, ion, or particle of matter is necessarily under tension and always tends to become discharged. In discharging, it always gives up energy to an external body through which the discharge takes place. I believe there is no known exception to this statement. The converse is also always true, that, when a body receives an electric charge, or, to express it in a different form, when two bodies become oppositely electrically charged or receive positive and negative charges, such bodies always simultaneously receive energy from the source of the electric charges. Electrically charged bodies are necessarily in a higher energy state than the same bodies not electrically charged, and always constitute a source of electrical energy. The discharge of electrically charged ions, or the neutralization of such ions by giving up their charges to electrodes constituting the terminals of any electric conductor or circuit, can occur, therefore, only by the ions simultaneously giving up electrical energy to that circuit.

There is an important fact in connection with the theory of electrochemical action, which, judging from its relation to the dominant hypothesis, does not appear to have ever been recognized. This fact is that in no electrochemical reaction does any ion ever give up energy to an electric circuit or to any other body in the

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so-called process of discharging or giving up its charges to an electrode and ceasing to be an ion, that is, by becoming an atom or molecule. On the contrary, every atom in passing into an electrolyte and becoming an ion does give up energy to some other body.

In the electrochemical reaction of the Daniell cell,

$$Zn + ZnSO_4 + CuSO_4 = ZnSO_4 + ZnSO_4 + Cu,$$

the Zn changes from an atom to an ion and the Cu changes from an ion to an atom. In this reaction the Zn loses chemical energy which appears in the electric circuit as electrical energy, while the Cu receives chemical energy at the expense of the electrical energy of the circuit. There are no other ions deposited or formed in this case. We cannot say that in this reaction an ion of SO_4 is deposited or ceases to be an ion or that it is in any way "discharged" or "neutralized," for it is in exactly the same condition before and after the reaction. There is no detectable difference between the SO_4 of $ZnSO_4$ and that of $CuSO_4$.

What has been stated of the relation between the energy changes and the ionic changes in the above reaction is true of every electrochemical reaction; namely, when an atom becomes an ion it always gives up energy and its energy condition becomes lower; when an ion becomes an atom it always absorbs energy from without, either the chemical energy of an adjacent body or electrical energy from the electric circuit, or both, and its energy state always becomes higher.

Whenever two ions are set free electrolytically at the opposite electrodes of any electrochemical system, that is, when they change from ions to atoms, these ions always absorb electrical energy from a source external to the electrolyte in this process, and the atoms so formed are in all cases capable of combining again and giving up this energy in forming ions. There is a great difference between electrolytically *setting-free* atoms and electrolytically *separating* them.

When we electrolytically decompose H_2SO_4 between platinum electrodes and liberate H_2 and O, these substances are set free and change from ions to atoms. Such an operation always absorbs electrical energy. When we electrolytically decompose H_2SO_4, using a cathode of PbO_2 and an anode of Pb, we *separate* H_2 from SO_4, but neither of these substances is *set free,* that is, no ion is changed to an atom. The reaction is

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$$PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O,$$

the SO_4 being an ion in $PbSO_4$ as well as in H_2SO_4, the H_2 and O being ions in H_2O as well as in H_2SO_4 and PbO_2, the lead being an ion in $PbSO_4$ as well as in PbO_2. Therefore, no ions have been changed to atoms. On the contrary, in this reaction an atom of Pb has been changed to an ion of Pb in forming one molecule of $PbSO_4$. This atom in changing to an ion gives electrical energy to the circuit and the cell is a source of electrical energy. The reaction described is that of discharging a lead accumulator. In reversing this reaction (charging the accumulator) an ion of Pb is changed to an atom of Pb, and this change necessarily absorbs electrical energy.

Whenever an electrochemical reaction changes an atom into an ion at one electrode, and an ion into an atom at the other electrode, the atom which changes to an ion adds electrical energy to the circuit at that electrode, and the ion which changes to an atom absorbs electrical energy from the circuit at the other electrode. If the change from the atomic to the ionic state of the one substance corresponds to a greater energy change than the change from the ionic to the atomic state of the other substance, the total electrochemical change adds electrical energy to the circuit and the cell is a galvanic battery, while, if the change from the atomic to the ionic state corresponds to a smaller energy change, the reaction will absorb electrical energy.

Since electric charges are always sources of energy and give up energy to the body through which they discharge, and since the ions of an electrolyte in changing to atoms never give up energy to, but always absorb energy from, a source external to the electrolyte in which the chance occurs, the conclusion seems to me unavoidable that ions cannot be electrically charged bodies; that, on the contrary, they are bodies which have a definite capacity for becoming charged from an external source as they pass out of the electrolyte and become atoms.

It seems to me that our conception of electrolytic dissociation should be reversed and that ions should be considered as devoid of electrical charges, but having a capacity for receiving electric charges, the maximum capacity of any univalent ion being 96,540 coulombs. When the ions become charged with this quantity of electricity from an external source they separate and become atoms.

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I have stated this objection to the theory of electrolytic dissociation to several eminent advocates of the theory, but have never received any refutation of it. The favorite method of avoiding this issue is to reply that these electric charges on the ions are not electric charges in the *ordinary sense,* and that there is an unknown or mysterious something which is capable of explaining it.

To assume that ions are electrically charged atoms obeying the laws of such charged bodies, for the purpose of explaining how these ions conduct electric current and how they carry a certain definite number of coulombs of electricity, and then to say that these charges are not electric charges, but mysteries, in order to avoid the logical sequence of the assumption, seems to me a confusion rather than a theory.

The first requirement of a credible theory is that it must not contradict itself. It may be at variance with all other theories, not excepting the theory of gravitation or that of conservation of the energy and matter, and it may, nevertheless, be credible and plausible, provided it is better able to account for the facts and is consistent with itself. It may even be inconsistent with many known facts and still be acceptable. No theory can be acceptable to reason, if it is not consistent with itself, or if one of its essential elements is mystery. Mystery is a universal theory in itself, which explains to the satisfaction of some minds all facts and phenomena without the aid of assumptions or necessity of mathematics. If mystery alone is an all-sufficient theory, why should we labor to build a theory consisting of only one part mystery and five parts mathematics, which contradicts itself and then does not account for the facts?

MR. CARL HERING (Communicated): I have always understood, and believe it is generally so understood, that ions are ions only as long as they form the electrolyte itself, and the moment they are deposited, set free, or combine with the electrode they cease to be ions and become atoms or molecules; they then cease to conduct the current electrolytically. I therefore cannot agree with Mr. Reed when he says that the lead in an accumulator plate is an ion. The lead simply combines with the ions and in that way the amount follows Faraday's Law, but because it follows this law it does not follow that it is an ion. A platinum plate will combine with some of the hydrogen ions, but that is no reason

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for saying that the platinum is an ion in the electrolysis of water.

MR. LOUIS A. PARSONS (Communicated): Mr. Reed's argument is logical and clearly presented, and if all the premises are true, the conclusion in regard to ions and electrons in an electrolyte would seem to be amply justified. But if we accept the hypothesis that atoms are charged and ions uncharged, how are we going to deal with the case of the ionization of gases? Will the hypothesis cover the cathode rays, Becquerel rays, the ionization of gases by X-Rays, ultra-violet light, etc.? Certainly, the proof that cathode rays are charged particles is conclusive enough, and if they are atoms, how does it come that the mass is the same for all gases and only the thousandth part of the mass of a hydrogen atom? Are the Becquerel rays then also atoms? What then are the ions? The electronic hypothesis covers conduction in metals, liquids, and gases, explains the Hall effect, the Kerr effect, cathode, Lenard and Becquerel rays, X-Rays, and ordinary light radiations, absorption and anomalous dispersion, the Zeeman effect, and other phenomena. The objections raised, it seems to me, could apply only to the single case of electrolytic conduction in liquids, and the new hypothesis is proposed to explain this case alone. Would it not be better to hold on to the theory having a vastly wider application, until it is shown beyond any reasonable doubt that it is incapable, even when modified, of explaining the single case, than to abandon it for a hypothesis better explaining this case, but limited to it? Perhaps, however, this new hypothesis can be made to explain these other phenomena, but I am unable to see how it can.

But would the new hypothesis better explain the phenomena of electrolytic conduction in liquids? If the ions are uncharged, how can we explain their migration through the liquid in the direction of the electric force?

It is in the point of the energy relations alone that the new hypothesis seems to be superior. If charged particles always have more electrical energy than uncharged particles, if this applies to ions and atoms, and if ions in solution always have less energy than atoms, the conclusion is evident. But let us look at this more closely. I hesitate to criticize Mr. Reed's statement that "when an atom becomes an ion it always gives up energy, and when an ion becomes an atom it always absorbs energy from without."

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Watson,[1] however, says "the intrinsic energy of ionized Zn is less than that of an equal mass of electrically neutral Zn, while the opposite is true in the case of Cu. The tendency of Zn to ionize and of Cu to become neutral, as exhibited during the working of a Daniell cell, follows naturally from these results." Arrhenius[2] also says, "as a rule, heat is evolved when ions are formed, that is to say, the heat of ionization is negative." He gives a table of heats of ionization from which it appears that ionization produces a decrease in the intrinsic energy in the case of K, Na, Li, Sr, Ca, Mg, Al, Mn, Fe (divalent), Co, Ni, Zn, Cd, Th and Sn, and increase in intrinsic energy in the case of Fe (trivalent), Cu (divalent), Hg, Ag and Pb.[3] This being true, if the old hypothesis fails to explain the facts in the case of the first set, the new hypothesis will fail for the second set, and is no more consistent within itself.

But I would go even further than this and say that I am not prepared to admit Mr. Reed's principal premise nor agree with him in his application of it. How do we know that if we bring two "charged" particles together so that they are no longer charged that their energy must necessarily be less? Does that not involve an assumption as to what takes place in the passage between the two states of "charged" and "uncharged?" In the discharge of a Leyden jar, heat is produced along the path of a spark and energy is radiated as electric waves, and obviously the intrinsic energy is less when uncharged than when charged. But what justification is there for reasoning from this to the case of atoms and electrons? It seems to me, we may here make any assumptions that do not lead us into any inconsistency. The negatively charged ion we conceive as consisting of an atom with more electrons than are necessary to render it neutral, and a positive ion as one with a deficiency of electrons. In considering the energy of either we must consider the kinetic energy of the electrons, the mutual energy of the electrons and atoms, the kinetic energy of the system, the mutual energy of the system and any existing external electrostatic or magnetic field, and the mutual energy of the system and all other similar systems. In the neutral

[1] Watson: "Text-Book of Physics," p. 846.

[2] Arrhenius: "Text-Book of Electrochemistry" (translation). Longmans, Green, and Co., 1902, p. 239.

[3] For Zn it is —16,300, for Cu +8,800, and Pb +509 (small calories).

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molecule there is no mutual energy of the system with other systems or external fields, but there is the kinetic energy of the system, the kinetic energy of the electrons, the mutual energy of electrons and atoms, the mutual energy of the atoms, and the mutual energy of the electrons. Is it then absolutely impossible that the "electrical energy" (whatever that may be) of the molecule should be greater than that of the ion?

Consider two Pt electrodes dipping in an H_2SO_4 solution in water and connected to a source of electromotive force. This electromotive force we shall think of as causing electrons to pass along from atom to atom in the opposite sense to the "direction of the current." Owing to the nature of the metallic circuit, free progress is impeded and work must be done to cause this transfer. As a result, we have an excess of electrons on the negative plate and a deficiency on the other. An external electrostatic field is thus produced in the liquid which causes the ions to move towards the oppositely charged electrodes. H ions, with a deficiency of electrons, move toward the excess of electrons on the negative plate. In some way an H ion receives electrons from the Pt ions until it has an excess instead of a deficiency (it is not discharged), and then unites with another H ion to form an H molecule. There has been an entire redistribution of the energies involved and I do not see that it is self-evident that the energy has been increased or that it has been decreased. And we must know that, before we can know whether energy has been added to, or taken from, the circuit.

JOHNS HOPKINS UNIVERSITY,
May 23, 1903.

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A paper read by title at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, President Richards in the Chair.

ON THE FORMATION OF NITRIC ACID BY ELECTRIC ENERGY.

By C. W. Volney.

When a mixture of dry nitrogen and oxygen is acted upon by the discharges of a strong secondary current, the formation of yellow vapors indicates the oxidation of nitrogen to peroxide.

If the reaction takes place in a closed vessel the quantity of peroxide produced is but small, amounting to a few per cent. of that which should have been formed by the material and energy engaged.

The process seems to be independent in the great measure of the time and energy of reaction.

It is generally considered that the oxide, NO, is the first product of the oxidation of nitrogen under the circumstances indicated, and that the yellow or brown gas accompanying this first reaction is therefore the result of the combining of the protoxide with pure oxygen to form peroxide.

At the same time it has been stated, since the time of Priestley and Faraday, that this nitrogen protoxide is decomposed by the electric current into nitrogen and oxygen, or into nitrogen and peroxide.

It is therefore well established that the nitrogen oxide, NO, is formed by electric energy and also decomposed by the same medium into its elements.

Buff and Hofmann[1] show that the discharge of the induction current decomposes the oxide very slowly; but through mercury or iron wire almost completely. These metals absorb nascent oxygen so that nitrogen, in the free state, results, and the oxides of the metals are formed, thus preventing the reversing of the reaction, *i. e.*, the forming of the oxide from the previously produced

[1] Buff and Hofmann: Ann. Chem. (Liebig), 113, 138.

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free elements. Grove[1] made similar observations, also Andrews and Tait.[2]

It will be seen that these quotations do not explain the cause of the narrow limits of the formation or of the decomposition of the nitric oxide in a closed vessel by electric energy; and even up to the present time I have not seen a report of experimental conclusions on this subject.[3]

As the formation of nitric oxide necessarily precedes that of nitric acid, an investigation of the causes of these limits is of sufficient interest to record the results of the following experiments:

The principal part of the apparatus consisted of a reaction flask of 1 liter capacity, mounted in the usual manner for admission and drawing off of gases and the introduction of platinum electrodes. It could be connected with apparatus for the absorption and measuring of the gases.

The electrodes discharged through a distance of 15 mm.; the current came from a transformer, giving 8 amperes and 8 volts. This produced in atmospheric air the characteristic yellow vapors inside of forty-five seconds and in nitric oxide gas inside of a minute, and was kept at these figures of measurement as evenly as possible during all the experiments, as the limits of the reaction were to be ascertained, as nearly as possible, under the same conditions. The determinations of nitrogen peroxide, NO_2, were made with N/10 permanganate solutions, the gas being absorbed by concentrated sulphuric acid. The nitric oxide gas was conducted, after passing through the sulphuric acid, into a measuring tube of 100 cc. capacity, filled with permanganate solution and standing in permanganate solution of N/10 strength. Nitrogen gas passed this and was collected in the measuring tube.

The nitric oxide gas was prepared from sodium nitrate by boiling with ferrous chloride solution and hydrochloric acid. The gas, for its purification, was conducted through caustic soda solution and collected in 8-liter (2 gal.) gasometer bottles, which contained some concentrated sulphuric acid at the bottom.

By pouring concentrated sulphuric acid into these gas-bottles, the dry nitric oxide gas could be driven over into the reaction

[1] Grove: Jahresbericht der Chemie, 1848, p. 326.
[2] Andrews and Tait: Proceedings of the Royal Soc., 1860, p. 247.
[3] Muthmann and Hofer: Ber. d. chem. Ges., 1903, p. 438.

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flask. Three series of reactions were observed under the electric discharge, for five, ten and twenty minutes.

FIVE MINUTES.

Peroxide found. mg.	Nitrogen found. cc.
25	5.3
35	7.3 or 7.5
23	5

The peroxide averaged 28 mg., corresponding to the decomposition of 27.3 cc. of nitric oxide.

TEN MINUTES.

Peroxide found. mg.	Nitrogen found. cc.
35	7.6
36	9
28	7

The peroxide averaged 33 mg., corresponding to the decomposition of 33.6 cc. of nitric oxide.

TWENTY MINUTES.

Peroxide found. mg.	Nitrogen found. cc.
35	8
30	7
36	8.5

The peroxide averaged 37 mg., corresponding to the decomposition of 35.8 cc. of nitric oxide.

The nitrogen found corresponds fairly well with the quantities of the peroxide.

The result may be expressed by saying that the same electric energy decomposes in five minutes, 2.73 per cent., in ten minutes, 3.3 per cent., in twenty minutes, 3.58 per cent. of nitric oxide gas into peroxide and nitrogen.

It may be inferred from the foregoing figures, that the decomposition expressed by the conventional

$$2NO = NO_2 + N$$

is followed by

$$2NO_2 = N_2O_4,$$

$$N_2O_4 = NO + NO + O_2,$$

and this by

$$NO + O = NO_2,$$

and also by

$$N + O = NO,$$

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and that this recurring reaction causes the limitation of the electric influence.

The examination of the products of the electric discharges on nitrogen peroxide or tetroxide offered considerable difficulties. For the purpose of obtaining a liter of perfectly pure peroxide vapors, I used the peroxide gas from nitrate of lead at red heat; the nitrate had been pulverized and dried for a long time at 90°-100°, and vapors were conducted, passing over pieces of molten caustic potash into the above-described reaction-flask, leaving this through a glass tube into the open air. This was continued until the gas, passing into concentrated sulphuric acid, was entirely absorbed, leaving in the absorption tube no sign of unabsorbed gas.

The discharge of the electric current of equal voltage for twenty minutes caused the before-described changes in color within the sphere of reaction, changing the space between the electrodes from white-greenish, into a light yellow and very dark brown.

After cooling, the gas was slowly drawn through sulphuric acid and was completely absorbed, except 1.7 cc., which proved to be nitrogen, and which probably was left inadvertently in the reaction-flask. The process showed the complete absence of nitric oxide gas. That, however, a reaction took place, was evident from the moving color spheres in the flask, and it may be assumed with good ground, that in the flask and within the sphere of the electric energy, here also the peroxide dissociated into oxide and oxygen and probably the following series of reactions followed each other: (1) $N_2O_4 = NO_2 + NO_2$; (2) $NO_2 = NO + O$; (3) $NO + O = NO_2$; (4) $NO_2 + NO_2 = N_2O_4$. I did not repeat this experiment, as I did not, at the time, see my way clear to determine any decomposition of the tetroxide.

The formation of nitrogen trioxide and pentoxide from nitrogen and oxygen in the dry state, or from the oxide and peroxide, by electric energy, is out of the question. The anhydrides of either are at the common temperature completely unstable, and decompose at all temperatures over 15° into oxide and oxygen and into peroxide and oxygen, and their formation at high temperatures is, therefore, inconceivable. The weakest electric current will separate therefrom peroxide and oxygen. The highest oxidation product, which can be effected by electric energy with dry nitrogen and oxygen, appears to be the tetroxide.

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The reaction of electric discharges in dry atmospheric air and enclosed space, should in a large measure comply with the foregoing observations. The yellow vapors which appear shortly after the beginning of the discharges indicate the formation of oxide and peroxide; the oxide can not be recognized or determined, as an excess of oxygen is invariably present, but it is very probable that its formation always precedes that of peroxide. The great excess of nitrogen may moderate or retard the reactions, but the formation of trioxide and pentoxide is excluded on the same grounds as previously adduced.

Treating dry atmospheric air in the reaction-flask, in the same manner as the nitric oxide, gave in three operations of ten minutes' duration each, 4 mg., 5 mg., 3 mg., or 4 mg. on an average, which corresponds to not quite 1 per cent. of the theoretical quantity of tetroxide obtainable.

It is very probable, that this very small yield may be increased by changes in apparatus and manipulation, but I believe that the whole result of these experiments shows the occurrence of oxidation and deoxidation processes, under the influence of the electric discharges and high temperatures, and that therefore the reaction in a closed space will be always a very limited one.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

UNIFORMITY IN ELECTROCHEMICAL EQUIVALENTS.

By Carl Hering.

The rapid development of the electrical science and industry was due in no small degree to the early establishment of a uniform, clearly defined and rational system of units, the ohm, volt and ampere. These units were first defined in terms of the so-called absolute system, after which concrete standards were adopted to correspond as nearly as possible to them. But as these concrete standards were only the closest approximation possible at the time of their adoption, their values had to be changed from time to time, and will probably continue to be modified; while these changes are accompanied by some inconvenience, yet this is infinitely less objectionable than uncertainty and lack of uniformity would be, in fact, there are comparatively few persons who have been inconvenienced by such changes made during the past twenty years, and fewer still would even notice any that may be made in the future.

It has thus been found that as long as absolute accuracy is impossible, the establishment of some uniform values is far preferable to continued uncertainty and to the use of different constants for the same thing by different persons or in different countries.

In electrochemistry there exists at present a very annoying lack of uniformity in the very constants used in most calculations, namely, in the electrochemical equivalents. This we owe largely to the chemist, as these constants involve the atomic weights which still seem to be uncertain to such a degree that many different values are in common use, each chemist claiming that his set is the more correct. Moreover, the values adopted by authoritative bodies of chemists are changed from time to time, and the variations are still so great that what the electrical engineer would call accuracy may well be said to be illusory.

In view of the fact that accuracy seems hopeless at present, is it not best to at least enjoy the next best thing, which is uniformity?

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Such uniformity is well within our reach, and would mean nothing more than the adoption by electrochemists of a combination of certain values already adopted by authoritative bodies. The American Chemical Society, to which we may well leave the subject of atomic weights, has adopted a set of these weights, which were presumably selected by and from the best authorities. By adopting these same atomic weights we are not only taking the best that such a national society can find, but we establish a much-desired uniformity between the chemists and the electrochemists, as far as atomic weights are concerned.

The International Electrical Congress of 1893, and subsequently a number of governments, including our own, have formally adopted a uniform value for one electrochemical equivalent, that for silver, namely, 0.001118 gram per coulomb. For the electrochemist to adopt any other value would be to disregard that which is legal, and which has been considered by the best authorities of different nations to be at present the nearest possible approach to the absolute value.

The object of the present paper is to urge electrochemists to adopt, for the present, this value and the above-mentioned set of atomic weights, which, taken together, give a complete set of electrochemical equivalents. By doing so there would be not only a much-desired uniformity among electrochemists themselves, but their values would agree with those of the chemist and would be in accord with the one existing legal value.

Even more than this, such electrochemical equivalents would then correspond with the figure which is now almost universally used for the ionic charge, namely, 96,540 coulombs per univalent gram-ion. This charge, when calculated on the above-mentioned basis, is 96,538.5, which, when cut down to four significant figures, which is all, if not more than the basic figures warrant, becomes 96,540.

Having such a set of carefully calculated electrochemical equivalents, the values for any particular element could then be readily changed from time to time by mere proportion, when a more reliable atomic weight is found for that element. The electrochemical equivalent of hydrogen on this basis is 0.010441 milligram per coulomb. It is evident that the much-discussed question of whether one should take $H = 1$ or $O = 16$, does not enter in the electro-

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chemical equivalents as they are the same for both, being constants of nature or actual weights per coulomb, which are entirely independent of any arbitrary system of relative weights. The customary ionic charge, however, is based on O = 16.

At present the ionic charge is a derived quantity which has been calculated from the atomic weights and the electrochemical equivalents. It may not be unreasonable to believe that, as this is a constant for all the elements, the most accurate determinations of the atomic weights may ultimately be made by means of it, in which case the conditions would be reversed, as the atomic weights would then become the derived quantity and the chemist would then have to come to the electrochemist for the best determinations of the atomic weights.

DISCUSSION.

PROF. W. D. BANCROFT: Mr. President, Mr. Hering has stated that we should take 1.118 milligrams as our unit, because it was the legal one, and because it was that accepted by the best authorities. It is true, of course, that it is a legal unit, but the recent experiments of Richards have shown that this value varies with the form of the voltameter used, and if you allow for the inaccuracies in the voltameter used by the different experimenters, their results all come back to the same figures, and so far as one can judge, the form of voltameter devised by Richards himself, is the one which is most free from error. Under these circumstances the value becomes 1.1175 instead of 1.118, and the value for the equivalent weight is approximately 96,600 (96,580). I think it would be a very great misfortune, in making a decision at this time, to select a value which we know to be wrong, simply because it is the legal value, and because it was the best value at the time it was done. We do not use the legal ohm because we know it is legal; we use the international ohm because it represents the closest approximation to fact which we have been able to get. It seems to me that the same principle applies in the case of the coulomb.

MR. CARL HERING: The difference in the electrochemical equivalent to which Dr. Bancroft called attention is only four-hun-

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dredths per cent. Now, there are very few experiments in electrochemistry that are made with such accuracy that this difference becomes noticeable. It seems to me, therefore, that the difference between 1.118 and 1.1176 is of interest only in very accurate physical research.

MR. A. H. COWLES: The figure is easier to remember when you have it an even 96,600.

MR. HERING: In all but very refined research it would make no difference whether we used the figure 96,500 or 96,600; the difference between them is only one-tenth of 1 per cent.

MR. COWLES: I think it would be a good suggestion if our society were to adopt the symbols and letters that are used to indicate different electrical quantities that are adopted by the American Institute of Electrical Engineers. In various text-books on electrochemistry there are different systems to represent different electrical quantities, and if we could bring ourselves to uniformity in that respect, I think it would be a great advantage.

MR. HERING: The international ohm is the ohm which is legal now. This illustrates the very point made in my paper, that is, that we have in the past changed the value of our ohm several times, in accordance with more accurate determinations of its real value; similarly, as long as we have no absolutely accurate values for the electrochemical equivalents, why not adopt universally the best we have at present, for the present, and then change them after we have more accurate ones which have been legally adopted or generally accepted, just as was done in the case of the ohm?

As to the statement of Mr. Cowles, it should be understood that if we adopt hydrogen as 1, we change that figure to 96,540, because that applies to oxygen = 16.

PRES. RICHARDS: Mr. Hering's suggestion of adopting a uniform value—96,540—would be equivalent to chemists adopting professionally a uniform relation between the atomic weight of oxygen and hydrogen. I do not think any chemist desires to have a legal definition of what the atomic weight of hydrogen is, oxygen being 16, or of what oxygen is, hydrogen being 1. I think it rather petrifies matters, and I should prefer to see the matter constantly revised, according to the best of our information, as we are revising constantly the atomic weights, or the relation of the atomic weights to each other. I think, to put it tersely, I

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would prefer to see frequent change in the values which we use, provided they are always as accurate as we can get them, rather than inaccurate uniformity.

MR. HERING: It seems to me that these differences are so extremely small that they really do not concern ninety-nine out of a hundred of the calculations made in practice. Most of the calculations are made by the ordinary experimenter or the industrial electrochemist, and to him it makes absolutely no difference whether that figure is 1.118 or 1.1176. In most cases it does not even make any difference to him whether he uses the figure 100,000 instead of 96,540, as the difference is only 3½ per cent.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

ELECTROMOTIVE FORCE OF ALLOYS.

By Wilder D. Bancroft.

As has already been pointed out by Ostwald and others, an alloy should show against a solution the potential of the less noble phase, and measurements of electromotive force should give us valuable information in regard to the number and nature of the solid phases. While this holds for certain pairs of metals, the method has not proved as serviceable as was hoped. Part of the difficulty is due to the fact that some compounds show potentials that differ but little from that of one of the pure metals. This source of error has been recognized. There is another to which I wish to call attention. In order to get the electrodes as nearly homogeneous as possible, they are cast; but the question then arises whether the cast electrode is in a state of stable equilibrium. In many cases it is certainly not. Slow cooling does not always lead to a state of stable equilibrium. In the cooling-curves for copper and tin alloys, as made by Roberts-Austen, we find signs of the eutectic in the alloy containing 55 per cent. Cu, while it should have disappeared as soon as the alloy contained a little more than 34 per cent. Cu. This discrepancy is due to the fact that the solid alloy, as actually prepared, consisted of Cu_3Sn, CuSn and Sn, instead of less Cu_3Sn, more CuSn, and no Sn.

This difficulty will be serious only in case the solid phase which appears at the higher temperature is the more noble with respect to the solution in which the measurement of electromotive force is to be made. Unfortunately, this is very often the case. There are then two ways of getting around the difficulty. One is to take a solution in which the metals reverse their usual position, the other is to anneal the alloy just below the proper quadruple point until equilibrium is reached. In sulphate or chloride solutions copper is more noble than tin. The reverse is the case in cyanide solutions. Unfortunately, we have not yet been able to get any

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satisfactory measurements of electromotive forces with bronzes in cyanide solutions. We have therefore had to anneal the bronzes and make measurements against tin in stannous chloride solutions. So far as we have gone the results have been eminently satisfactory. Alloys containing over 65 per cent. Sn show no potential difference against tin, whether annealed or not. Alloys containing 45 to 65 per cent. Sn show a difference of potential against tin when annealed and no difference when not annealed. The first group consists of mixtures of CuSn and Sn. The second group consists of Cu_3Sn and CuSn when equilibrium is reached. On rapid casting there is free tin present, as shown by the experiments of Roberts-Austen and confirmed by the electromotive force measurements made in my laboratory.

So long as we are not certain that we are studying a system in a state of equilibrium, all conclusions based on density determinations, electrometric measurements, microscopic examinations, heats of reaction, tensile strength, electrolytic conductivity, etc., are liable to error. Conversely, the interpretation of such properties becomes simpler and more accurate, provided we are certain that we are investigating states of equilibrium.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

ELECTROLYTIC PRODUCTION OF METALLIC COMPOUNDS.

BY C. F. BURGESS AND CARL HAMBUECHEN.

An accurate estimate of the importance and extent of industrial development of electrochemistry is difficult to make. It is interesting and important to note that an estimate based upon achievements as recorded in the literature, is materially different from that based upon the capital invested in successful industrial enterprise. If all that is claimed in print could be realized in practice, the electric current, through its electrolytic and thermal properties of producing chemical change, would be of much greater service to mankind than it is now, even after the enormous strides have been made in this direction. Progress will be made in the near future through the realization of published though at present unpracticed claims, as is self-evident from a study of achievements of the past two decades. Advancement of known laboratory experiments to industrial processes affords ample room for a continuation of development in electrochemical lines even though no new scientific discoveries be made.

The voluminous literature in this comparatively new field is a most useful tool for the student of applied electrochemistry, provided it is properly used. The knowledge, however, as to how it should be used is most difficult to acquire. A statement might be warranted that an investigator will make almost as much progress by neglecting the literature as by following its guidance implicitly. The ability to use this tool properly lies in the power of discriminating as to the truth of published statements, which, in turn, requires a thorough knowledge of the laws of nature.

There is probably no field of industrial activity in which such a large percentage of the literature relating to it possesses the properties of inaccuracy, incompleteness, and absolute untruth as does applied electrochemistry. This condition arises through various characteristics of the writers, including excessive enthusiasm lead-

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ing to premature declaration, incomplete knowledge of the subject under treatment and even the apparent intent to mislead the public. The patent literature is especially characterized in the exhibition of these traits, and as printed frequently bears internal evidence of the leading scientific and technical societies. Erroneous statements published, perhaps in all sincerety, by over-enthusiastic or insufficiently informed observers are almost invariably allowed to stand uncorrected, largely through the natural reluctance which one has of admitting that he was wrong, and by reason of that same trait of humanity which causes a man, after he emerges from the tent of a side-show where he has been swindled, to allow his neighbor to pay his money and enter without a word of warning.

One of the greatest advantages which could accrue to this industry in which we are all interested would be the placing of the literature on a basis of greater reliability. The difficulties, however, in accomplishing it are comparable in extent to those which must be overcome in the deposition of aluminum from aqueous solutions, which problem has been solved so many times on paper but not in practice.

Electrochemistry being a new and little understood field, has been a fertile one for fraudulent schemes. A list of such would be a lengthy, interesting, though perhaps a familiar one. A similar list of electrochemical applications which have been published through no fraudulent motives, but which have failed through unforeseen conditions, would be much larger; and it is a noteworthy fact that our literature is almost entirely lacking in publications setting forth the reasons for failure of previously supposed successful processes. Such publications would be of especial value as a guidance to others and would be of advantage in promoting industrial progress by calling attention to problems which need solution, such problems as an experimenter could discover otherwise only by lengthy preliminary research.

This somewhat extended introduction has been entered into not only for the purpose of calling attention to some unfortunate conditions in which we are interested, but also as a justification for the paper on the subject here presented, on the electrolytic production of metallic compounds.

It is not the purpose of this discussion to present an ideal or even an improved process for producing metallic compounds, but

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rather to point out the limitation of the methods at present available and to deal with some of the difficulties which must be encountered in large scale working.

The use of electricity in producing compounds of the metals seems to have been alluring to experimenters. Appended hereto is a partial bibliography of the literature of the past ten years relating to this matter, but there are few statements giving the reasons for the failure of many of the processes to attain commercial importance.

Electrical energy suitably applied to a soluble sulphate, chloride, nitrate or similar salt of one of the alkali metals, may produce a dissolving action upon a metal anode with a consequent production of a salt of that metal similar to that which would be produced by ordinary chemical corrosion by a corresponding acid. It is from this fact that arises the commercial possibility of replacing acids commonly used, by cheaper substances. Thus in the production of metal sulphate or chloride it is cheaper to obtain the SO_4 or Cl from a sodium salt than from the acid, especially in such localities where, by reason of freight rates or other circumstances, the acid may be of relatively high price.

A metal nitrate may be produced much more economically from sodium nitrate than from the nitric acid as far as cost of material is concerned. Figured on the basis of NO_3 content, 1.35 pounds of sodium nitrate is equivalent to 1 pound of nitric acid and, at present market values, represents a relative cost of 2.7 cents and 8 cents. Similar relative values might be shown in other cases.

Compensating for this saving in the cost of materials is the cost of power necessary in electrolytic operations, but where the process can be carried out on a large scale, this cost can be made insignificant. The amount of energy necessary to decompose 1.35 pounds of sodium nitrate in the production of a metal compound will be in the neighborhood of one-quarter horse-power-hour, which, at a cost of 0.5 cent, makes the cost per pound about 0.15 cent. A further advantage for the electrolytic process is the possibility of recovery of valuable cathode products, one of which, in the case above considered, is 0.6 pound sodium hydroxide, representing a value considerably more than the cost of power.

To realize the advantages for electrolytic methods which such

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reasoning makes apparent, requires suitable design of electrolytic apparatus, and it is on this point that the ingenuity and skill of the designer is required, inasmuch as each case presents individual characteristics and demands special treatment. The necessary complications of such apparatus may, with justice, be urged as favoring the purely chemical methods; but as partially or even more than offsetting this disadvantage is the fact that from a given metal surface corrosion may usually be caused to take place with much greater rapidity through the aid of electric current than without. This produces economy of floor space and volume of apparatus.

The metal compounds which may be produced may be classified as soluble or insoluble in accordance with the dissolving power of water for them. The chemical method for producing soluble metal compounds is typified in the action of an acid on a metal, either directly or indirectly, and the insoluble metal compounds may be produced from solutions of the former by precipitation by a carbonate, hydroxide or other precipitating agent. The double decomposition thus taking place results in the formation of a soluble salt as a by-product, which is usually of such a nature as to be difficult to recover in a pure state with an expenditure of energy sufficiently low to warrant it.

As compared with such chemical method, the advantages which can be obtained by the electrical current are the following: The dissolving acid and the precipitating base may be replaced by a cheaper salt, which is made by the electrical current to exert the dissolving action at the anode with the simultaneous formation of an alkali product at the cathode and the subsequent union of these two products producing a precipitate with a regeneration of the original salt. This salt may be used over again and does not represent a waste product. There is, therefore, no expensive material required to be consumed. While the electrical energy is a factor which must be taken into account, it is a comparatively unimportant one in figuring the cost of production on a large scale.

To the corrosion of lead and the production of various lead compounds much attention has been given, from the electrochem-

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ical standpoint, due to the possibility of attaining the advantage of electrolytic over chemical methods in the greatest degree and on account of the unlimited demand which exists for such products. Associated with the production of white lead is the record of many failures of electrolytic methods, and the chemical methods still maintain control in spite of various promises to the contrary.

The following discussion will relate more particularly to the treatment of metallic lead, though the conclusions derived from the study of this metal may apply to the treatment of various other metals.

One of the principal processes which has been employed for the production of a lead hydroxide is one in which the pig lead is used as the anode in a solution of sodium nitrate with a copper or other metal cathode. Faraday's Law tells us that 3.8 grams of lead should be dissolved for every ampere hour; that 1.48 grams of sodium hydroxide should be formed at the cathode for the same current and that a mixture of these two products will form 4.45 grams of lead hydroxide with the regeneration of salt which was first decomposed. Assuming a current density of 20 amperes per square foot of anode surface, which is within the limits of possibility, the rate at which the lead will be removed or corroded is almost 80 grams per square foot per hour. The rapidity with which a metal may thus be made to corrode indicates one of the advantages claimed by electrolytic methods.

Unfortunately for practical operation, the reasoning as previously outlined is not sufficient, and the process is far from being as simple as might at first sight be supposed. In the first place, it will be found that the corrosion at the anode does not take place in an ideal manner, lead nitrate is not produced in such quantities as the application of Faraday's Law would indicate, and the discrepancy is accounted for by the formation of other basic lead compounds which are insoluble or partially so. The formation of such undesired compounds may result in a waste of the lead, the introduction into the solution and the desired product of impurities, the partial or complete insulation of the anode and consequent increase in the amount of power, and the uneven corrosion of the metal which it is desired to transform.

In the case of sodium nitrate as the elctrolyte, the reaction at

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the cathode is not simply the primary liberation of sodium and its secondary reaction with water to form sodium hydroxide and liberate hydrogen, as has been assumed by various authorities, but other secondary reactions occur which must be taken into account. Observation of the fact that little or no hydrogen may be liberated at the cathode would lead to an investigation as to what actually occurs, and it is found that the reducing action which such hydrogen exerts, causes the sodium nitrate to be reduced to nitrite, then through its lower forms with the final production of ammonia. This resulting action causes the solution to become alkaline and explains what at first sight might appear as a surprising fact, namely, that the current efficiency in the production of alkali is greater than 100 per cent.

For the production of lead hydroxide by the mixing of the anode and cathode products within the cell, even though the anode could be evenly and satisfactorily corroded, a difficulty would be introduced in the production of this excess of alkali which is as follows: The alkaline solution acting on the lead hydroxide which has been precipitated, redissolves some of it, forming a plumbate and thus introducing lead as a soluble compound in the solution. The natural effect of a current passing through this compound is to deposit the lead upon the cathode, which is done in such a manner as to produce a loose, non-coherent, spongy mass of lead which is easily detached and contaminates the product, decreases the efficiency, and may even result in short-circuiting the cell.

Further, the production of nitrite at the cathode results, through the diffusion of this substance to the anode, in the formation of a nitrite of lead and basic lead compounds, which increases the difficulty, heretofore mentioned, of unsatisfactory corrosion of the anode. The production of ammonia which, escaping into the air, may be a source of annoyance, also represents a waste material, for the sodium nitrate is consumed in direct proportion as nitrogen escapes from the solution, either in the form of nitrogen or ammonia.

It will be self-evident then that the solution remaining after the cell has been in operation for some time, is decidedly different in its chemical composition from that used at first.

To cause this electrolytic process to operate as is desired, re-

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quires a design of the electrolyzing apparatus in such a way that the difficulty heretofore mentioned can be avoided or taken into account. It has been the purpose of some investigations which have been carried out in our laboratory, to determine what these conditions are. The principal features which require attention in this process and which are typical of a considerable class of operations, are the followng:

The Anode.—It is desired that the current efficiency of corrosion be 100 per cent., with the formation of no secondary and undesirable products. To attain this, requires careful attention to various factors, such as the purity of the anode, its physical structure, current density, density and chemical nature of the electrolyte.

In the case of a lead anode and a sodium nitrate electrolyte, the NO_3 radical should unite with the lead to form a soluble lead nitrate. A practical trial demonstrates the fact that to obtain this compound to the exclusion of other lead compounds, such as the oxide or basic lead salts, we cannot employ an alkaline or even a neutral solution. Such other compounds result in the formation of a coating which often has the appearance of a thick mud attached to the surface. The clean corrosion and 100 per cent. efficiency in lead nitrate formation can be attained by having a small amount of free acid in the neighborhood of the anode. Our experience has shown that an acidity of 0.1 normal nitric acid will enable this satisfactory corrosion to be realized on lead plates carrying a current as high as 20 amperes per square foot. This characteristic of corrosion applies not only to lead, but to various other metals.

Cathode.—The reactions at the cathode should be carefully studied to determine qualitatively and quantitatively the reduction products there formed. The proper choice of a cathode depends, to a certain extent, upon what these substances are, and the material should be such that no cathode corrosion can take place.

The Electrolyte.—It is on the proper choice of the electrolyte that the success of the process depends more, perhaps, than on any other factor. It influences the character of the corrosion, the character of the primary and secondary electrolytic products, the amount of power necessary, and the cost of keeping the solution

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in working condition. In the case of lead corrosion, we are limited to the choice of such electrolyte materials as those whose anion produces, with lead, a soluble lead salt. This indicates the nitrates and acetates among the cheaper materials, and the chlorides and chlorates, which are less satisfactory on account of higher resistance and lower degree of the solubility of resulting salts.

It will be evident that to overcome the difficulty of contaminating the precipitate with impurities formed at the anode, all that is needed is to draw the solutions from the electrolytic tank and, after having passed them through a filter, cause the precipitation to take place in another vessel. In the same manner the dissolving action of the cathode solution on the resulting precipitate could be avoided by adding just enough of the cathode solution to cause complete precipitation of the anode products. To realize these conditions requires the complete separation of the two electrode products while in the electrolytic cell. This can be accomplished by means of diaphragms.

While the single diaphragm, Fig. 1, separating the anode from the cathode will serve in some classes of electrolytic work, it will not serve in this process, the objection being that the solutions of different character existing on either side of such diaphragm cause precipitation to take place within the diaphragm and a consequent clogging of the same. To avoid this the electrode products may be kept completely separated by the use of two diaphragms as illustrated in Fig. 2. The stock solution feeding the cell is introduced between the two diaphragms and the electrode solutions are drawn off from their respective compartments. Diffusion of the electrode solutions is prevented by maintaining a positive flow of solution through the diaphragms toward the electrodes at such a rate as to counteract any tendency for diffusion. To maintain a sufficient rate of flow requires a definite difference of pressure, which may be produced by maintaining the level in the various compartments at different heights, as indicated in the figure. This method of separation has been described in a patent by A. B. Browne, U. S. Patent No. 563,553.

In the experience of the writers it was found that maintaining a proper difference of level involves a difficulty. When the cell is first placed in operation, the density of the solutions in the various

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compartments is practically the same and to maintain a given rate of flow requires a definite difference of level, depending on the

FIG. 1.

FIG. 2.

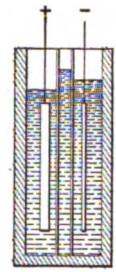
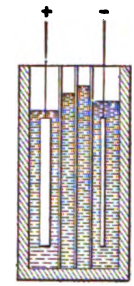


FIG. 3.



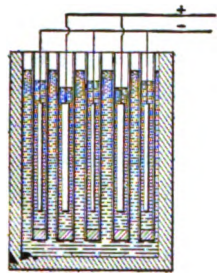


FIG. 4.

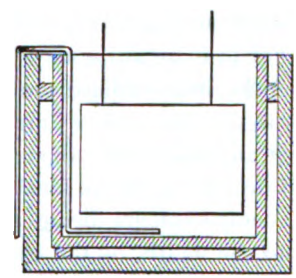


FIG. 5.

character of the diaphragm. After electrolysis takes place for some time, the density of the solution in the anode compartment increases and that in the cathode compartment decreases or remains practically the same. The effect of the increase of density in the anode solution results in an equality of pressure toward the bottom of the cell, although there may be a difference of level at the surface of the solutions. This results in the diffusion of the anode solution into the intermediate and thus into the cathode compartment. To obviate this, an adjustment of the levels of the solutions to correspond with the relative density should be made. Another variable factor is the change of the character of the diaphragm due to the influences of the solution and the chemical products upon the same. A light, firm canvas has been found to give very satisfactory results, but the alkaline cathode solution and

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the acidified anode solution act in different degrees upon the two diaphragms in changing the porosity and the rate of diffusion. Temperature and current density also influence this diffusion. The maintaining of a definite fixed difference of level of solution between various compartments is hardly a satisfactory method of operation.

The writers have found that by a very simple method this difference of levels can be automatically adjusted by keeping the level of the solution in the intermediate compartment constant and drawing from the electrode compartments a certain definite *volume* of solution per unit of time. If the rate of diffusion with a given difference of level is not sufficient to supply this volume, the difference of level increases to such an extent that the flow through the diaphragm will be sufficient.

The fact that the lead solution in the anode has a higher density than the solution in any other of the compartments, makes it necessary either to maintain a very large difference in the level of the anode and the intermediate compartment, or the construction of the electrolytic cell with a limited depth. Our experience has shown that an anode plate about 8 inches in depth was the largest that could be used with the kind of diaphragms described.

Anode compartments being limited in depth in the manner shown, and the width, by the construction of the cell and the diaphragm, to about 2 feet, and the anode current density being limited for reasons of satisfactory corrosion and economy of power to about 10 amperes per square foot, the solution which should be drawn from every compartment is, in an hour's time, a comparatively small quantity. One liter per hour is a rate found desirable and for a uniform flow of this amount requires a very small opening in the discharge tube. On account of the difficulty of entirely preventing the formation of insoluble particles in the solutions, these openings gave a great deal of trouble from clogging, requiring constant attention until another method of regulating the discharge was devised.

In Fig. 6 is illustrated the manner in which the outflow can be satisfactorily regulated. Instead of regulating the flow by the size of the opening of the siphon tube O, the opening is made large enough to allow any precipitated particles to readily pass through. This outlet, normally closed by a piece of rubber pressing against

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it by a spring S, is opened periodically by an eccentric, H, rotating

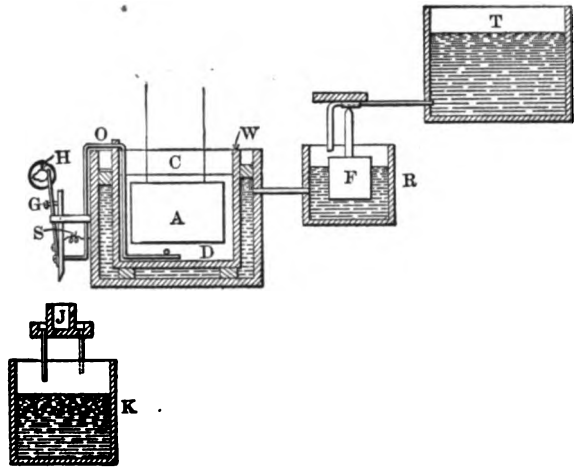

FIG. 6.

at a fixed speed. The quantity of solution drawn off is regulated by adjusting the screw G. Fig 7 illustrates a number of such

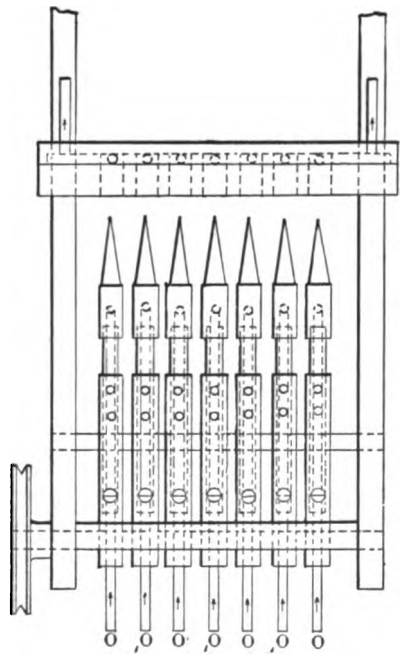

FIG. 7.

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outlets arranged on a tank having three anode and four cathode compartments. This method of regulation proved satisfactory, and may be advantageously used in various other electrolytic processes. It was found that in the operation of a solution of sodium nitrate having a density of 1.12 sp. gr., 0.6 per cent. of free nitric acid was desirable to insure satisfactory anode corrosion. This free acid can be introduced either in the stock solution flowing between the two diaphragms, or directly into the anode solution. In the former method there is more uniform distribution of this acid than in the latter, but where the stock solution is acidified there is involved the disadvantage that more acid is required by some of it going into the cathode compartment and thereby being neutralized. To overcome this disadvantage a third diaphragm may be introduced, as shown in Fig. 3, the stock solution flowing into compartment E being acidified to the proper amount, and the stock solution flowing into compartment F being neutral. This prevents the unnecessary consumption of acid.

Figure 8 is a photograph taken from a small laboratory plant for the corrosion of lead. The electrolytic tank has three anode and four cathode compartments and is capable of corroding about 10 pounds of lead per twenty-four hours. Fig. 6 is a diagrammatic representation of the same equipment, where T is the tank containing the stock solution, R the regulating device for maintaining a constant level of solution in the electrolyzing tank, A a lead anode, and D a canvas diaphragm placed around a wooden frame, W. The top part of each diaphragm is paraffined to prevent a flow of the solution through the portion not completely immersed. O is a siphon tube for drawing off the lead nitrate solution as it is formed. The solution flows into trough J, which is so constructed that the anode and cathode solutions are kept separated, and thence it flows into tank K.

With this construction the diaphragms can be readily removed from the electrolytic cell when renewal and cleaning is necessary.

By the above method continuous operation can be effected with high percentage of corrosion, no clogging of diaphragms, and with uniformity of composition of solution running from the cell. The electromotive force found necessary is about 1.4 volts, representing an expenditure of energy of 0.22 horse-power-hour per pound of lead corroded.

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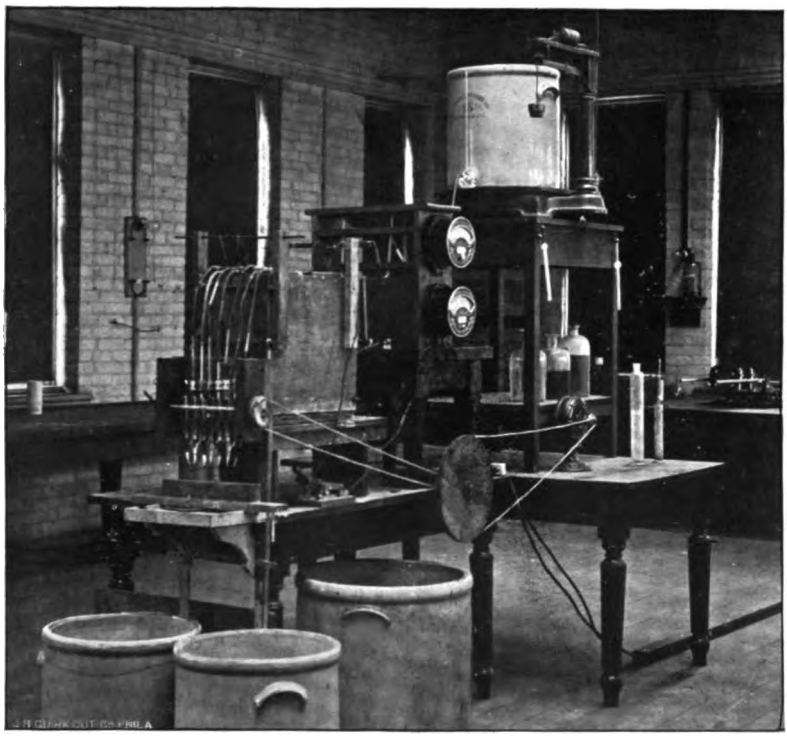

FIG. 8.

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Various methods of procedure may be followed in utilizing this apparatus for commercial purposes. A method of manufacturing white lead from such solutions which has been extensively described in the literature, consists in mixing these two electrode solutions to form a lead hydroxide and thereby a "regeneration of the original solution." The precipitate of lead hydroxide thus formed was treated with CO_2, either from the air or generated chemically, changing the precipitate to a lead carbonate, which is the useful white pigment. Analysis of the cathode solution, however, shows that the claim of "regenerating the original solution" cannot be realized, on account of the formation of ammonia and nitrite compounds. An analysis of the cathode solution on one run showed the following content per liter:

	Grams.
$NaOH$	25.0
NH_4OH	3.52
$NaNO_2$	0.165
$NaNO_3$	54.3

A similar analysis of the anode solution showed a content per liter of

	Grams.
$Pb(NO_3)_2$	113.5
$NaNO_3$	57.6

The anode solution might be used to advantage for the manufacture of lead nitrate by fractional crystallization, but to do so requires the recovery of the values in the cathode solution, and it is upon this point that commercial success depends. By heating to a boiling temperature, the ammonia can be driven off and recovered, but the separation of the nitrite, the nitrate and the hydroxide cannot be readily accomplished.

In all methods for the production of metal compounds from a sodium nitrate electrolyte, the question of commercial success seems to depend upon the suitable treatment of the cathode solution, either by separating the materials or by finding uses for the solution as it comes from the electrolyzing tank. If the sodium nitrate fed into the electrolyzing tank could be completely utilized, the problem of the treatment of solutions could be considerably simplified, but in order to keep the electrode products completely separated in the electrolyzer it was found desirable to run the solu-

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tions at such a rate that about one-half the sodium nitrate passes through without undergoing electrolysis.

Some of the disadvantages attendant upon the use of sodium nitrate, as the electrolyte material, can be avoided by the use of sodium acetate. The amount of alkali produced at the cathode is equivalent to the lead acetate formed at the anode and the chemical reactions are, therefore, simpler. The relative advantage of the acetate is not determined by this factor alone. The cost of sodium acetate is much greater than that of the nitrate, calling for great care in the prevention of waste from leakage, and washing the precipitate. The acetate requires to be used in a considerable degree of purity, while the ordinary commercial grade of sodium nitrate is sufficiently pure. The voltage necessary is considerably higher and the difficulty in effecting clean anode corrosion is decidedly against the acetate.

The experiments here described were carried out in an attempt to test, on a laboratory scale, various processes which have been described for the production of white lead. The work was carried on for several months, and we have found that it is entirely possible to produce a white lead of exactly the same composition, as far as the relative amount of hydroxide and carbonate of lead are concerned, as in the old Dutch process. The physical properties can also be duplicated. The conclusion seems to be justified, however, that there is little chance for the electrolytic process replacing the chemical methods for the production of this useful pigment, at least along the lines referred to. From the present market values of pure lead and the white lead made therefrom, it is seen that there is very little margin to pay the cost of the electrical energy, the necessary losses in the electrolyte, the cost of casting the lead into shape suitable for anode purposes, labor and depreciation of the electrolytic tanks and leave anything for a profit.

In the production of various other lead compounds, however, there seems to be greater opportunity for commercial application of the electrolytic method. The acetate of lead may be produced in a manner similar to that suggested for the production of the nitrate; lead chloride may be produced from the electrolysis of a hot sodium chloride solution, the lead chloride separating out on cooling; lead chromate, which is a pigment used in large quantities, can be made by precipitating the anode solution by

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sodium bichromate, thereby regenerating the original solution and furnishing the free acid necessary for effecting uniform corrosion of the lead anode.

It will be noted that in all of the proposed processes for the electrolytic production of metallic compounds, electricity plays only an incidental and sometimes very minor part in the operation. There are undoubtedly many places where the electrolytic step might be advantageously introduced into the present purely chemical operations. Not only may the electrolytic effect of the current be utilized, but the heat effect may also be employed. A process for the production of metallic compounds utilizing the heat properties of the current consists in volatilizing the metal either in a resistance or arc furnace and exposing the vapors or the fine metal particles thereby produced to the action of chemical reagents which will produce the desired chemical compound. The controlling factor in this case is the cost of electrical energy, the amount of energy required to treat a pound of metal in this way being much greater than in the electrolytic methods.

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DISCUSSION.

PRES. RICHARDS: I have done some experimenting myself in producing insoluble metallic compounds from the metals used as anodes. I have tried the manufacture of white lead and found that one of the great difficulties in manufacturing a fine quality of white lead is the dropping of metallic particles from the anodes in with the precipitates; and this is dependent very largely upon the current density used at the anodes. If too high a current density is used the action is similar to that of a concentrated acid upon an easily soluble metal, tearing it to pieces, and small particles of metal then drop in and contaminate the product which is being obtained. I find, by regulating properly the current density, that the white lead can be obtained without any specks of metallic lead in it, whereas, by using too high a current density, it is contaminated with specks of metallic lead. I would also call attention to the easy manner of making a metallic sulphide by means of using the metal as an anode, in a solution of sodium hyposulphite. It makes a very pretty lecture experiment to use a cadmium anode in a solution of sodium hyposulphite; after passing the current for a little while, cadmium sulphide commences to form, with its beautiful golden yellow color. At first there is very little precipitate because cadmium sulphide is soluble to a certain extent in the electrolyte; but after passing the current for some time the electrolyte becomes saturated with cadmium sulphide and then a precipitate forms very abundantly. It is a quick and easy way of making sulphides. I do not know to how many metals it may be applicable. I have tried it with four or five. I think there is a great field for manufacturing the insoluble compounds of metals by the use of appropriate solutions; at least there is a great field for experimenting in that line.

MR. CARL HERING: I have been very much interested in this paper, as I think there is a great future in the manufacturing of some chemical products by means of electrochemical reactions as distinguished from chemical reaction. I also agree with Professor Richards in regard to the current density, only I would rather put it in this way: that it is very important to keep the solution which you wish to have acted upon in actual molecular contact with the electrode and not let it be

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separated from them by an exhausted molecular layer; that is to say, if you want to use a strong current density you must have very strong circulation. I think this is a very important factor in a great many of these reactions, and that it is not fully appreciated. I have made some experiments in that direction myself and I have been surprised to see what great improvements are produced by very rapid circulation.

PROF. W. D. BANCROFT: I am sorry that this paper could not have been discussed more in detail by some of our technical friends. It would be of great assistance to those of us who are connected with the universities if our efforts at teaching our students something about applied electrochemistry could be subjected to friendly criticism by those who have had an opportunity to test these things on a large scale.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, President Richards in the Chair.

SINGLE POTENTIALS OF ZINC IN AQUEOUS SOLUTIONS.

By Harrison Eastman Patten and William Roy Mott.

INTRODUCTION.

The authors present in this paper a series of single potentials of zinc in typical aqueous solutions, together with decomposition voltages of some of the solutions used, especially the sulphates. Measurements of residual current have been made for a number of solutions; in some cases the figures given by other experimenters were confirmed and in others a magnitude for the current density was obtained one hundred to one thousand times as great as any found in the literature.

METHOD.

1. *Single Potential Determination.*—A normal electrode as figured and described in LeBlanc's "Electrochemistry" was used. Its electromotive force was taken as —0.56 volt; this was checked against a second half cell and found to balance perfectly. Connection was made between the normal electrode and the cell containing the solution to be tested against zinc, by a siphon from the normal electrode and by a strip of moistened filter paper from the cell. These connectors both dipped into a third vessel containing an electrolyte (usually an aqueous solution of sodium carbonate). In this third vessel the cell itself was placed, and by heating or cooling this outer vessel temperature coefficients could be determined. The electromotive force of the chain, normal electrode—solution—zinc, was determined by the usual compensation method, using as a zero instrument a Queen galvanometer: a deflection of ¾ of a scale division was produced by a millionth of an ampere. The readings were generally accurate to 0.005 volt.

2. *Decomposition Point Determination.*—The method of determining the electromotive force-current curve was essentially that suggested by Bancroft.[1]

[1] J. Phys. Chem., 5, 133 (1901).

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We used a glass cell with fused-in polished platinum electrodes, 1.2 cm. wide by a little less than 2.5 cm. long, and placed parallel about 7 mm. apart. Fig. 1 gives the cell complete. The design of this cell is due to Prof. Kahlenberg. The electromotive force current curves were obtained by electrolyzing solutions in this cell, and reading volts on a carefully calibrated Jewell 3-volt voltmeter, and milliamperes on a good Weston milliammeter.[1] The temperature of the cell was controlled by a large water-bath.

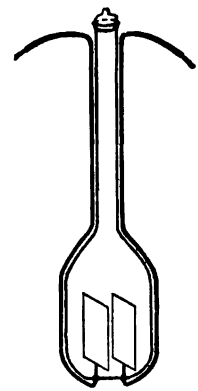

Fig. 1.

PART I.

Relation of single potentials of zinc in various solutions to the single potentials of zinc in these same solutions mixed half and half with normal $ZnSO_4$.

Our values of the single potential upon which the discussion is based are given in Table I. Column I contains the chemical formula of the dissolved substance, the concentration being indicated at the left by *n*, and being generally normal. Column II gives the single potential in volts of carefully polished zinc in these solutions. Column III represents the departure of the single potential in volts from the representative value which is given in Column II. Those spaces left blank represent, as far as our observations go, time-effects not exceeding 0.01 volt. Column IV represents the maximum difference in volts between different specimens of zinc in the same solution. Column V represents the single potential of zinc in the mixture, half and half, of the solution with normal $ZnSO_4$.

[1] Kindly furnished us by Professor Kahlenberg.

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TABLE I.—ZINC SINGLE POTENTIALS.

	I.	II. Solution 25° C.	III. Time variation.	IV. Specimen variation.	V. $ZnSO_4$ mixture 25° C.
n	HCl	+0.494			+0.497
n	HI	0.523			0.514
n	HNO_3	0.371			0.396
n	H_2SO_4	0.458		0.009	0.480
n	KOH	0.938	0.030	0.015	0.902
n	NaCl	0.509			
n	KF	0.458			0.514
2*n*	KCl	0.523	0.009	0.045	0.514
n	KBr	0.500			0.517
n/10	KI	0.438	0.009		0.557
n	KCN	0.967			0.882
n	KCNO	0.825	0.021		0.650
n	KCNS	0.551			0.537
n	$K_4Fe(CN)_6$	0.514			0.543
n	KNO_3	0.353			0.410
n	KNO_2	0.226			0.443
n	K_3PO_4	0.574	0.063		0.523
n	Na_2SiO_3	0.797	0.060		
n	K_2CO_3	0.571	0.240		0.557
n	K_2SO_4	0.551	0.021		0.537
n	$MgSO_4$	0.500			0.520
n	$ZnSO_4$	0.528		0.015	0.528
n	$CdSO_4$				0.478
n	$FeSO_4$				0.478
n	$CuSO_4$				0.472
n	Na_2WO_4	0.217	0.222		0.514
n/3	$KMnO_4$	0.090	0.156		0.438
n	K_2CrO_4	0.147	0.225		0.444
n	$K_2C_4H_4O_6$	0.605	0.006		0.518

The results as given in Table I are charted in Plate I.

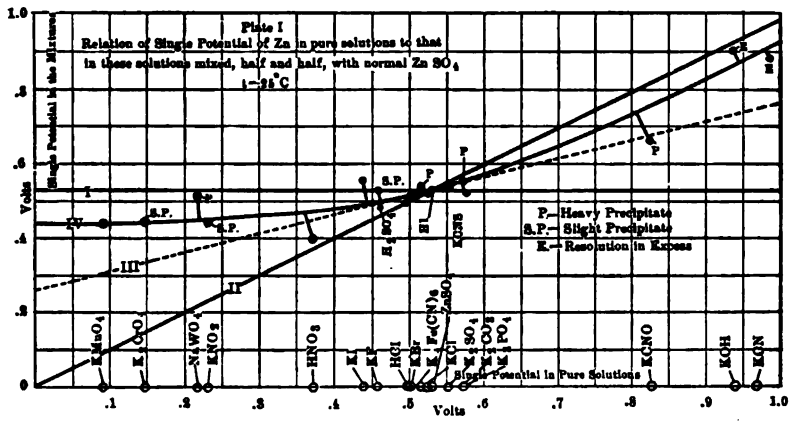
Plate I
Relation of Single Potential of Zn in pure solutions to that in these solutions mixed, half and half, with normal Zn SO4
t = 25° C
Single Potential in the Mixtures
Volts
P.—Heavy Precipitate
S.P.—Slight Precipitate
R.—Resolution in Excess
Single Potential in Pure Solutions
Volts

PLATE I.

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Abscissae are single potentials of zinc in the solution given, expressed in volts; ordinates are single potentials of zinc in a mixture (50 per cent. by volume) of the same solution (represented on the abscissa) with normal $ZnSO_4$.

Curve I gives the single potential of zinc as it would be if only $ZnSO_4$ were effective, since in that case the value would be constant (+ 0.528 volt) and would be represented graphically by a straight horizontal line. Curve II shows what values of the single potential might be expected if $ZnSO_4$ had no influence upon the single potential, since for each value of the single potential plotted there would be the same abscissa and the same ordinate. If the ordinate and abscissa scales were the same the line joining the plotted values of the single potential would make an angle of 45° with the axis and would go through zero. Curve III represents the trend of the single potentials if the resulting values were mean proportionals between those in $ZnSO_4$ and in the solutions mixed with it. Curve IV was obtained by drawing a smooth curve through the points given by our experimental data in Table I. Curves I, II, and III are drawn upon the assumption that the concentration changes consequent upon mixing the electrolytes cause negligible change in the single potential. This is justified by the fact that simple dilution with water from normal to one-half normal solution causes very slight change in the single potential.

DISCUSSION.

(1) *Law of Mixtures.*—Single potentials of zinc in mixtures show that the predominating influence rests with that acid radical which by itself gives the highest single potential.

This law is analogous to that which holds good in the case of single potentials of alloys toward solutions: that the observed single potential of the alloy is controlled by the metal in the alloy highest in the electrochemical series. For example, amalgams. Both of these laws are in accord with the law of maximum work.

(2) A striking exception was found by us in mixtures of $KMnO_4$ and K_2CrO_4 where the single potential of zinc was much lower than in either solution alone. However, addition of $ZnSO_4$ or sulphuric acid to this mixture gives a single potential but little lower than that in $ZnSO_4$ or in sulphuric acid. We tried many

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mixtures of 1/3 normal $KMnO_4$ with 1/3 normal K_2CrO_4; similarly, mixtures of 1/30 normal $KMnO_4$ with 1/30 normal K_2CrO_4. In every mixture the single potential of zinc was more negative than in either chromate or permanganate alone. The lowest value obtained was —0.83 volt.[1]

(3) The single potential of zinc in solutions of acids, bases and alkali salts varies greatly. The limits are from +1 volt (KOH and KCN) to even —0.80 volt (in certain peculiar solutions of the powerful oxidizing agents $KMnO_4$ and K_2CrO_4). There is, however, a general centralization of values about +0.52 volt and the percentage of the total number of determinations (Column II, Table I) which fall within 0.10 volt either way from +0.52 volt (that is, between the limits of +0.42 volt and +0.62 volt) is a little over 50 per cent.

(4) Oxidizing reagents, as would be expected, tend to give low values; for example, $KMnO_4$, K_2CrO_4, KNO_3, KNO_2, etc.

(5) The so-called solution tension of zinc is seen from these curves, Plate I, to be a peculiarly varying quantity.

(6) Other influences that must be considered are:

(*a*) In K_2CO_3, Na_2WO_4, $KMnO_4$ and K_2CrO_4, as seen in Column III, Table I, there are such large time-effects as to complicate the problem.

(*b*) Temperature coefficient: At a given temperature a few degrees change shows slight effect in the single potential. We observed no marked regularities in the temperature coefficients.

(*c*) The maximum variations for our specimens, of which 4 or 5 were tried, were between 0.005 and 0.045 volt, depending upon the solution used.

(*d*) In many of the mixtures chemical reaction interferes; we have precipitates and therefore large changes of concentration. In K_2CrO_4, KNO_2, and KF mixed with $ZnSO_4$ there is, as we would expect from the table of solubilities given in "Fresenius," some slight precipitate but not sufficient to vitiate the results. In the Na_2WO_4, $K_4Fe(CN)_6$ and KCNO the precipitation was so complete that the single potential in the mixture has little significance as regards the law of mixtures. In the case of KOH and KCN the mixtures were made up to exact resolution of the precipitate first formed. On Plate I, P stands for rather complete

[1] The authors have in hand data bearing upon this point which will be communicated in the near future, probably through the columns of *Electrochemical Industry*.

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precipitation; S P for only a slight precipitation; and E for exact resolution of precipitate in excess of the solvent. A slight acidity or basicity would exert considerable influence upon the single potential.

PART II.

DECOMPOSITION POINTS.

1. Methods of Determining Decomposition Points.

A. A galvanometer in series is used to note the point when continuous current begins to flow.[1] This method is totally unsatisfactory because of the residual currents. We have measured values of the residual current in many solutions with impressed voltages less than 1 volt. Some such solutions were normal H_2SO_4, HI, KCN, KCNO, KCNS, $K_4Fe(CN)_6$, 1/30 normal K_2CrO_4, 1/30 normal $KMnO_4$, etc., etc. In no case was the residual current lacking.

B. The use of a voltmeter to note the voltage at which products of electrolysis first appear.[1] (1) A microscope facilitates the observation of minute gas bubbles. (2) The first trace of metal is best determined by dipping the rinsed cathode into an acid and noting whether hydrogen is evolved.[2]

This second method, B (not (2) under B), gives decomposition voltages that harmonize well with the decomposition voltages calculated from the usual thermal data, which assumes the separation or formation of these products.[3]

C. The discharge potential method may be described as impressing an electromotive force upon a cell, suddenly interrupting the current and quickly reading the counter electromotive force developed in the cell.[4]

D. Following the suggestion of Bancroft,[5] we have taken the decomposition point as the intersection of the CR line (produced) with the axis of ordinates. However, we are in doubt as to the exact point he had in mind from which the CR line is to take its rise.

[1] Le Blanc: "Elements of Electrochemistry, page 246, Macmillan and Co., 1896.

[2] F. W. Küster: Zeit. Electrochem., 7, 257, November, 1900.

[3] The heat of formation used is not that calculated necessarily from the elements, since the elements are frequently not the products of electrolysis. For example, in electrolyzing $ZnSO_4$, the heat of combination should be calculated for the *union in solution of the products* Zn, free oxygen and SO_3.

[4] "Electrochemical Polarization," John W. Langley, Trans. Am. Electrochem. Soc., Vol. 2, p. 255 (1902).

[5] J. Phys. Chem., 5, p. 133 (1901).

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2. *Experimental Results.*

Table II contains electromotive force-current curves for various electrolytes. The number of each curve is given at the head of its column, likewise the symbols indicating the composition of the solution used. These same numbers are placed upon the curves as drawn in Plate II. In the table, V stands for volts, and A for amperes.

TABLE II.—DECOMPOSITION-POINT CURVES.

1. $ZnSO_4$.		3. $ZnSO_4$. $MgSO_4$.		2. $MgSO_4$.		4. $CdSO_4$.	
V.	A.	V.	A.	V.	A.	V.	A.
1.50	0.001	2.70	0.004	1.00	0.0005	1.09	0.001
1.85	0.002	2.90	0.016	1.30	0.001	1.41	0.001
2.45	0.005	3.00	0.032	1.52	0.001	1.87	0.0015
2.54	0.006	3.30	0.060	1.72	0.0015	2.08	0.0015
2.67	0.013	3.50	0.083	2.00	0.0015	2.43	0.017
2.77	0.021	4.00	0.125	2.20	0.003	2.58	0.033
3.00	0.045	4.50	0.180	2.38	0.007	2.94	0.085
3.50	0.117	4.50	0.200	2.82	0.030	3.80	0.220
4.00	0.190	4.00	0.145	3.22	0.073	4.30	0.300
4.67	0.280	3.50	0.085	3.67	0.135		
		3.00	0.075	4.30	0.251	$t = 25°$	
$t = 25°$		2.50	0.000	4.60	0.300		
		$t = 22°$ C.		$t = 25°$ C.			

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TABLE II.—(*continued*).

5. $CdSO_4$. $ZnSO_4$.		6. $FeSO_4$.		7. $FeSO_4$. $ZnSO_4$.		8*a*. $FeCl_3$. $FeSO_4.(NH_4)_2SO_4$.	
V.	A.	V.	A.	V.	A.	V.	A.
2.00	0.0025	0.50	0.001	0.50	0.0105	0.20	0.011
2.36	0.008	0.75	0.003	0.60	0.0025	0.40	0.020
2.50	0.015	0.90	0.010	0.70	0.003	0.80	0.060
2.70	0.037	1.30	0.025	0.80	0.003	1.00	0.147
3.00	0.070	1.73	0.054	0.90	0.0035		8*b*
3.00	0.070	2.88	0.059	1.00	0.0045	0.60	0.017
3.30	0.100	3.05	0.063	1.10	0.006	0.70	0.030
3.50	0.100	3.48	0.131	1.20	0.006	0.80	0.070
3.70	0.115	3.95	0.200	1.30	0.006	1.00	0.135
3.90	0.146	4.40	0.300	1.40	0.007	1.2	0.160
4.00	0.160			1.60	0.008	1.4	0.130
4.50	0.230	$t = 25°$		2.00	0.022	1.6	0.127
4.70	0.250			2.50	0.022	1.8	0.120
5.00	0.300			3.00	0.035	2.0	0.125
4.60	0.240			3.50	0.070	2.2	0.140
4.25	0.200			4.00	0.120	2.0	0.140
4.00	0.170			4.50	0.180	2.2	0.157
3.80	0.137			5.00	0.240	2.4	0.177
3.50	0.093					2.6	0.240
3.25	0.062			$t = 22°$ C.		2.8	0.300
3.00	0.034						
2.80	0.015					$t = 23°$ C.	
2.60	0.003						
2.50	0.0015						
2.00	B						
1.50	0.000						
$t = 22°$ C.							

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TABLE II.—(*continued*).

9a. $MgSO_4$. $ZnSO_4$. $CdSO_4$. $FeSO_4$. $CuSO_4$.		9b.		9c.		9d.	
V.	A.	V.	A.	V.	A.	V.	A.
0.40	0.003	4.70	0.277	0.50	0.002	0.50	0.003
0.90	0.010	4.60	0.264	0.60	0.003	0.60	0.004
1.00	0.013	4.50	0.250	0.70	0.005	0.70	0.007
1.10	0.017	4.30	0.230	0.80	0.007	0.80	0.010
1.20	0.019	4.20	0.197	0.90	0.011	0.90	0.012
1.30	0.015	4.10	0.187	1.00	0.011	1.00	0.014
1.4	0.013	3.90	0.155	1.10	0.011	1.10	0.014
1.5	0.013	3.80	0.140	1.20	0.011	1.20	0.012
1.6	0.017	3.70	0.130	1.30	0.010	1.30	0.012
1.7	0.020	3.60	0.115	1.40	0.010	1.40	0.012
1.8	0.025	3.50	0.100	1.50	0 010	1.50	0.012
1.9	0.035	3.40	0.087	1.60	0.012	1.60	0.012
2.0	0 039	3.00	0.050	1.70	0.017	1.70	0.020
2.1	0.042	2.50	0.030	1.80	0.023	1.80	0.025
2.2	0.042			1.90	0.030	1.90	0.030
2.3	0.040			2.00	0.037	2.00	0.039
2.4	0.039			2.10	0.040	1.90	0.020
2.5	0.039			2.20	0.040	1.80	0.015
2.6	0.043			2.30	0.040	1.70	0.014
2.7	0.050			2.40	0.040	1.60	0.012
2.8	0.060			2.50	0.040	1.50	0.011
2.9	0.070			2.60	0.040	1.40	0.010
3.0	0.080			2.70	0.050	1.30	0.010
3.3	0.095			2.80	0.058	1.20	0.010
3.5	0.109			2.90	0.070	1.10	0.009
4.0	0.160			3.00	0 070	1.00	0.009
4.5	0.237					0.90	0.007
						0.80	0.006
						0.70	0.005
						0.60	0.003
						0.50	0.002
				$t = 22.5°$ C.			

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TABLE II.—(*continued*).

10. H_2SO_4.		11. H_2SO_4. $ZnSO_4$.		12. $CuSO_4$.		13. $CuSO_4$. $ZnSO_4$.	
V.	A.	V.	A.	V.	A.	V.	A.
0.70	0.000	1.70	0.002	1.10	0.0005	1.50	0.002
1.44	0.0005	1.80	0.005	1.52	0.008	2.00	0.040
1.56	0.0005	1.90	0.010	1.55	0.008	2.50	0.104
1.93	0.006	2.00	0.020	1.71	0.020	3.00	0.127
1.97	0.008	2.20	0.047	1.84	0.040	3.20	0.145
2.16	0.040	2.40	0.077	2.33	0.098	3.50	0.165
2.29	0.068	2.60	0.110	3.00	0.237	3.70	0.185
2.56	0.147	2.80	0.130	3.35	0.300	4.00	0.220
2.84	0.300	3.00	0.147			4.30	0.257
		2.00	B	$t = 25°$ C.		4.50	0.267
$t = 25°$		2.50	0.002			4.70	0.300
		2.60	0.002			$t = 22°$ C.	
		2.70	0.006				
		2.90	0.027				
		3.00	0.067				
		3.10	0.110				
		3.30	0.165				
		3.50	0.280				
		$t = 22°$ C					

TABLE II.—(*continued*).

14. K_2SO_4.		15. K_2SO_4. $ZnSO_4$.		16. H_2O_2.	
V.	A.	V.	A.	V.	A.
1.10	0.001	2.00	0.000	0.24	0.003
1.61	0.0015	2.20	0.000	1.00	0.008
1.99	0.0015	2.40	0.000	1.50	0.011
2.48	0.010	2.60	0.006	2.00	0.013
2.74	0.036	2.80	0.020	2.50	0.019
3.20	0.081	3.00	0.040	3.00	0.022
3.40	0 130	3.20	0.063	3.50	0.025
3.70	0.200	3.40	0.095	4.00	0.028
4.10	0.300	3.60	0.125	4.50	0.033
		3.80	0.147	5.00	0.038
$t = 25°$		4.00	0.167	5.50	0.042
		4.60	0.240	6.00	0.045
		4.00	0.145	5.50	0.042
		3.80	0.115	5.00	0.037
		3.60	0.087	4.50	0.034
		3.40	0.060	4.00	0.030
		3.20	0.037	3.50	0.025
		3.00	0.011	3.00	0.020
		2.80	0.004		
		2.60	0.000	$t = 23°$	
		$t = 25°$ C.			

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3. *Curves.*

In Plate II are represented curves showing the relation between electromotive force and current mainly for a series of sulphates. In general, the solutions used were normal, and were the same in which the single potential of zinc was determined. The symbol of the salt whose solution was electrolyzed is given at the top of the plate along the zero-line from which the curve starts. Where two different symbols are given, a mixture of those salts, half and half, was electrolyzed. In some cases return curves were traced and the direction is indicated on the curve by arrows. Ordinates are in volts; abscissae in milliamperes, as indicated by the scale on the plate, except for H_2O_2 where the current scale is magnified ten times.

Curve 1. $ZnSO_4$. Slight bubbling noted at 2.67 volts may have occurred at a lower voltage.

Curve 2. $MgSO_4$. Gas begins to come off very slowly at 2.20 volts. Upon examining the diagram it will be noted that there are two CR drop lines which may be explained as due to heating effect.

Curve 3. Mixture, half and half, of $ZnSO_4$ with $MgSO_4$. This curve was taken after having passed 0.10 ampere for half a minute. This curve also shows the heating effect in that the return curve has much less slope and therefore there is less resistance. The decomposition point is also raised, probably by partial exhaustion of the zinc sulphate.

Curve 4. $CdSO_4$. The CR drop-line is very regular.

Curve 5. $ZnSO_4$ with $CdSO_4$, half and half. The curve at a current of one hundred milliamperes shows an almost vertical rise, the value of which is given in Table II. The metal plated out from this solution was by no means as readily dissolved by dilute sulphuric or nitric acids as was the zinc plated out of other solutions under similar conditions. The return curve does not show an abrupt drop. At 2 volts a negative value was obtained for the current. This is indicated by B, meaning that this is the point at which the cell would act as a battery.

Curve 6. $FeSO_4$. This curve is unique in that it has a large current flowing at less than 1-volt pressure, and in that at 1.7 volts the curve takes almost a vertical rise and has its last bend at the top of this rise.

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Curve 7. $FeSO_4$ with $ZnSO_4$, half and half. The values for the current given are averages of several curves. Indentations are noted in the curve analogous to those for $FeSO_4$ alone, but to a less marked degree.

Curve 8*a*. $FeSO_4(NH_4)_2SO_4 + FeCl_3$. This curve is peculiarly significant from the fact that it appears to start from zero voltage, and at 0.2 volt we have the very considerable current of 11 milliamperes passing. From 0.2 volt to 1 volt the values of the current given are those obtained upon the first electrolysis; from 0.60 volt to 2.20 volts the values of current are those obtained immediately after running the voltage up to 1 volt and back again; this branch of the curve is lettered 8*b*. The values of current given from 2 volts to 2.80 volts are those which check after running over the curve several times, although there is a small time-effect; this branch is lettered 8*c*. As the voltage is raised above 2 volts and then decreased, there is considerably less current flowing than went through the solution as shown by the first curve. But this current is still several milliamperes at 0.50 volt. The solution used was made up by saturating distilled water with an excess of solid ferrous ammonium sulphate and of solid ferric chloride.

Curve 9. The solution was made up of equal volumes of normal $MgSO_4$, $ZnSO_4$, $CdSO_4$, $FeSO_4$, and $CuSO_4$. The four sets of values given are selected from a series of twelve determinations of the curve. As might be expected, this curve is characterized by four abrupt changes in curvature. Branch 9*a* is the ascending curve, branch 9*b*, the return curve, crossing branch 9*a* and terminating at 2.50 volts. Branches 9*c* and 9*d* are the last two curves to the right on Plate II.

Curve 10. This is the curve for H_2SO_4.

Curve 11. $ZnSO_4$ and H_2SO_4. Values of current given for 1.70 volts to 3 volts represent those obtained upon the first electrolysis. After running between 100 and 150 milliamperes through the solution for two minutes, the current values given for 2 volts to 3.50 volts were obtained which check very well upon repetition; the lower decomposition point disappears after running over the curve once. Zinc plates out and holes were observed in the zinc coating where bubbles of hydrogen came off.

Curve 12. This is the curve for $CuSO_4$.

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Curve 13. $ZnSO_4$ and $CuSO_4$. This curve is distinguished by the very gradual change in curvature. It was noted that bubbles of gas came off at both electrodes, in considerable quantity, during electrolysis.

Curve 14. K_2SO_4.

Curve 15. $ZnSO_4$ and K_2SO_4.

Curve 16. H_2O_2. The hydrogen peroxide used, was the commercial solution containing between 2 and 3 per cent. H_2O_2. There was a copious evolution of gas upon both electrodes before impressing an electromotive force upon the cell.

4. Numerical Constants.

The numerical constants which fix the general form, curvature, asymtotic relationships, points of inflection, etc., have the following mathematical significance; if the curve be expressed algebraically the coefficients distributed through this equation would be functions of these first constants. For example, the coefficients of an algebraic equation in x and y representing the curve for such a mixture as $ZnSO_4$ with $CdSO_4$ (Plate II, Curve 5) are simple functions of the various constants and quantities which we have noted and deduced for that curve in Table III, which also contains data of a like character for the other curves.

The physical significance of each of these points on the curves (as in Plate II) should not be lost sight of in giving algebraic expression to the curve. Thus, we have to consider the following:

(1) The distribution of electromotive force between the electrodes and the distribution of the CR drops.

(2) The composition of the electrolyte both near the electrodes and between them.

(3) Resistance of electrolyte; *a*, of the stripped electrolyte near the electrode and *b*, of the products of electrolysis at the electrodes such as gases or solids (iodine, oxides, etc.).

(4) The heating effect; the distribution of this effect is directly proportional to the distribution of the resistance.

(5) The current density at both anode and cathode, and the factors which cause it to vary.

(6) Diffusion of the solute induced by partial stripping of the solution at the electrodes.

(7) The change in the products due to variation in the current

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density and hence the consequent change in the thermal data to be used in calculating the voltage of decomposition.

(8) Agitation of the electrolyte by gases evolved upon the electrodes during electrolysis.

(9) Increase in the voltage necessary for electrolysis due to the separation of hydrogen upon the cathode. This is the phenomenon studied by Caspari.[1]

(10) Energy relationships involved in the process of electrolysis as indicated by the area between the electromotive force-current curve (see Plate II) and axis of abscissa.

For the sake of comparison we have calculated the resistance of the electrolyte between the platinum electrodes used. These were 6 to 7 millimeters apart and had an area of 3 sq. cm. on each face, and were placed parallel as shown in the accompanying illustration. Using the formula

$$C = \frac{E}{R},$$

we found E by subtracting the polarization voltage of decomposition (V) from the voltage necessary to pass 100 milliamperes, through the cell. C is then 100 milliamperes, and we get immediately the value of R. In Table III we have summarized the essential points upon the curves in Plate II mainly from the standpoint of voltages.

The following description deals with the fundamental voltages of the curves.[2] V_0 is the polarization voltage of decomposition as determined by the intersection of the CR line (produced) with the axis of ordinates. The CR line used was the normal CR line of the electromotive force-current curve which corresponds ap-

[1] Ztschr. phys. Chem., 30, 90.

[2] We use the term "fundamental" to characterize constants that bear a simple relation to the coefficients in the algebraic or transcendental expression of the current electromotive force curve, and that are determined by the points of inflection, slopes, rates of curvature, etc., which follow from the physical conditions in the electrolytic cell. For example, in either of the general algebraic equations,

$$y = Ax^n + Bx^m + \ldots + C,$$
$$y = A f(x) + B f'(x) + C,$$

the fundamental voltages, as V_0, V_1, V_{CD}, EP, etc., bear a simple relation to A, B, C, etc., but not necessarily in the respective order given.

Jahn's expression for the excess electromotive force, induced by change of current density, may serve as an example of a transcendental equation,

$$P = \phi + \gamma \log_{10} I.$$

Where P = polarization electromotive force or current electromotive force, I = current density (Ztschr. phys. Chem., 29, 88 (1899)), ϕ = A magnitude of the voltage independent of the current density and therefore comparable to the decomposition voltage as given by LeBlanc and others, and γ = A proportionality constant.

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proximately to a current density of over 30 amperes per square decimeter. V_1 is the voltage required to pass 1 milliampere through our cell (for the given electrolyte) and corresponds to a current density of $^1/_3$ of a milliampere per square centimeter. V_3 is the voltage required to pass 3 milliamperes, and corresponds to a current density of 1 milliampere per square centimeter.[1]

V_{100} is the voltage required to pass 100 milliamperes, corresponding to $33^1/_3$ milliamperes per square centimeter. The current density in milliamperes per square centimeter in all these curves may be obtained by dividing the milliamperes (indicated on the abscissa) by 3, since the area of the electrodes was 3 square centimeters (see description of cell). $V_0 - V_3 = V_{CD}$, where V_{CD} represents the increase in voltage due to the change in current density from 1 milliampere per square centimeter to from 20 to 100 times that value.

In the case of mixtures, after reaching a certain current density for the compound with the higher decomposition point, the curve shows an abrupt change of curvature, and in Table III the volts for such a point are given under the head of "B. P. volts" and the amperes under the head of "B. P. amperes," where B. P. indicates break point. Under "T. P. volts" and "T. P. amperes" are indicated the volts and amperes for the point on the curve at the top of the rise.

In the case of mixtures we extended the CR line for the upper part of the curve back to its intersection with the axis of ordinates. This intersection gives a polarization value comparable with that similarly determined for the lower part of the curve. Subtracting the lower polarization value, given in column "B. P. P." from that just found for the upper part of the curve and given in column "T. P. P.", we get the excess voltage which the alloy of the higher metal gives upon plating out. This last value is given in the column "E. P." The value given in column V_0 for single salts coincides with that given in column "B. P. P." for mixtures.

Current density constants have been calculated for the break points and are of importance as to diffusion phenomena and

[1] We chose current densities of one-third of a milliampere per square centimeter and of one milliampere per square centimeter as close approximations to the point given by Le Blanc. This choice was necessary because our measurements of the current below the decomposition point (of Le Blanc) show that no such sharply defined point exists, although the electromotive force-current curve certainly has an abrupt curvature near this point.

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related phenomena, and as to the increase in chemical work which accompanies increase in current density.

The constants which follow from energy relations have not been tabulated. Two methods of using the data charted in Plate II are suggested: 1, calculating the energy efficiency for a given current density for each electrolyte used; 2, the determination of that current density for each electrolyte which will give a stated energy efficiency.[1]

For the convenience of the reader we repeat in condensed form the signification of the symbols used to head the columns in Table III.

V_0 = Volts, no current.
V_1 = Volts, 1 milliampere.
V_3 = Volts, 3 milliamperes.
V_{100} = Volts, 100 milliamperes.
V_{CD} = Volts due to current density.
T. P. = Top point.
B. P. = Bottom point.
B. P. P. = Bottom point polarization.
T. P. P. = Top point polarization.
E. P. = Excess pressure.

5. Discussion.

C. Decomposition:[2]

(1) Small residual current. In determining current-electromotive force curves we found, in common with previous experimenters (as was stated before), that below the decomposition voltage (as given by Le Blanc) a small current flows, and in some instances the current even appears to start at zero voltage. Consequently we consider in this section the subject of residual currents.

Among the earliest of these experimenters was Helmholtz. In 1873 he found that the residual current was less under diminished pressure, and on this basis rightly attributed the conduction to the presence of dissolved gases.[2]

Similar explanations have been put forward by others, especially in the discussion of the paper by Mr. Carl Hering, entitled "An Electrochemical Paradox," brought out at the second meeting of the American Electrochemical Society.[3] Kahlberg pointed out

[1] C. F. Burgess: "Efficiency of Electrolytic Vats," Elec. World, 32, 686.

[2] Ostwald: "Electrochemie," Chapter XVII; also Pogg. Ann., 150, 483 (1873); Wiss. Abhandl., 1, 823.

[3] Trans. Am. Elec. Chem. Soc., 2, 139 (1902).

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TABLE III.

		V_0.	V_1.	V_2.	V_{100}.	$V_{100} - V_0 = E$.	$R = \frac{E}{C}$ ohms.	$V_0 - V_2 = VCD$.	B.P. amperes.	B.P. volts.	T.P. volts.	T.P. amperes.	B.P.P.	T.P.P.	E.P.
1	$ZnSO_4$	2.62	2.20	2.41	3.38	0.76	7.6	0.21							
2	$MgSO_4$	2.95	1.52 to	2.25	3.54	0.50	5.0	1.44[1]							
		2.60	1.72		3.45	0.85	8.5	1.00[1]							
3	$MgSO_4$	2.70	2.55	2.64	3.72	0.98	9.8	0.06							
	$ZnSO_4$	2.80[2]			3.63	0.83	8.3	0.16							
4	$CdSO_4$	2.37	1.40 to 1.90	2.18	3.02	0.65	6.5	0.19							
5	$ZnSO_4$ $CdSO_4$	2.37	2.00 to 2.10	2.10 to 2.20	3.26	0.89	8.9	0.22	0.100	3.25	3.57	0.105	2.37	2.83	0.46
		[2]	2.50[2]	2.57[2]	3.56[2]	0.73[2]	7.3[2]	0.68[2]							
					3.50[2]	0.75[2]	7.5[2]	0.18[2]						2.75	
6	$FeSO_4$		0.50	0.75	3.19[2]	0.41[2]	4.1[2]		0.054	1.73	3.02	0.058	1.51	2.78	1.27
7[4]	$ZnSO_4$		0.45	0.75					0.006	1.10	1.40	0.006	1.02	?	?
	$FeSO_4$								0.022	1.80	2.84	0.022	1.54	2.68	1.14
					3.90[2]	0.75[2]	7.5[2]		0.022	2.84	4.05	0.122	2.68	3.00	0.47
9a	$MgSO_4$ $ZnSO_4$, $CdSO_4$ $FeSO_4$, $CdSO_4$,		0.20	0.40					0.020	1.18	1.90	0.035	1.06	1 75	0.69
									0.035	1.90	3.00	0.080	1.75	2.42	0.67
					3.75	0.72	7.2								
							7.2		0.080	3.00	4.00	0.160	2.42	3.03	0.61

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TABLE III.—(*continued*).

		V_0.	V_1.	V_2.	V_{100}.	$V_{100} - V_0 = E$.	$R = \frac{E}{C}$ ohms.	$V_0 - V_2 = V_{CD}$.	B.P. amperes.	B.P. volts.	T.P. volts.	T.P. amperes.	B.P.P.	T.P.P.	E.P.
	9*c*		0.50	0.55					0.011	0.90	2.00	0.035	0.82	1.81	0.99
									0.035	2.00	2.60	0.040	1.81	2.40	0.59
									0.040	2.60	2.90	0.070	2.40		
									0.070	2.90					
	9*d*		0.50	0.55					0.012	0.90	2 00	0.040	0.80		
8*a*	$FeCl_3 + (NH_4)_2SO_4$	1.70			2.08[3]	0.31[3]	3.1[3]						0.50 to		
	$FeSO_4$	1.60			0.90				0.140	1.00	2.30	0.170	0.56		
	8*b*			0.05					0.160	1.00	2.30	0.160			
10	H_2SO_4	2.00	1.70	1.85	2.40	0.40	0.40	0.15							
11	$ZnSO_4$	1.95	1.70	1.77					0.080	2.20	3.35	0.180			
	H_2SO_4	2.82[3]	2.60[3]	2.65[3]	3.35[3]	0.24[3]	2.4[3]								
12	$CuSO_4$	1.7 to 1.9	1.30	1.38	2.35	0.65	6.5	0.32							
13	$CuSO_4$	1.70	1.50	1.55	2.46	0.76	7.6	1.15	0.110	2.50	3.20	0.135	1.66	2.17	0.51
	$ZnSO_4$	2.2[3]			2.92[3]	0.72	7.2		0.180		3.70			2.33	
									0.160		3.50			2.28	
14	K_2SO_4	2.84	2.30	2.40	3.28	0.54	4.4	0.44							
	K_2SO_4	2.80	2.45	2.54	3.40	0.60	6.0	0.26	0.100	3.40	4.60	0.240	2.80	3.16	0.36
15	$ZnSO_4$	3.02[3]		2.80	3.68[3]	0.66[3]	6.6[3]	0.22							
16	H_2O_2	0.00	0.14	0.50				0.00							

[1] High current density effect probably due to heating effect.
[2] Return curve value.
[3] Values for higher branch of curve.
[4] Three changes of curvature noted for this mixture.

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in this discussion that Henry's Law rendered very plausible the explanation given by Bancroft for the reduction of electromotive force necessary to pass a current through dilute aqueous sulphuric acid between platinum electrodes, as the pressure was increased by the formation of gases in the electrolysis.[1]

Bigelow[2] has shown that for 0.005 normal H_2SO_4 in water with platinum electrodes 17 mm. square and 2.89 sq. cm. in area, and 11 mm. apart after 82 days with 1 volt constant pressure, the residual current fell to an apparent minimum of 0.169 microampere.

President Richards and Mr. Landis, in their admirable research presented April 16, 1903, to this Society, have given quantitative expression to the inter-relations between diffusion phenomena of gases in solution and the residual current. An especially interesting experiment was that in which water in a strong sealed glass tube resisted the passage of current between platinum electrodes under a pressure of 3 volts, but allowed a current to flow as soon as the sealing was broken. This absence of current, residual or otherwise, was illustrated in an extreme case by Burgess where he placed 70 volts on an aqueous solution in a strong steel bomb and found that the current which first passed quickly fell to zero. This absence of current he explains as due to the insulating action of the gases evolved upon the electrodes. This explanation probably applies to the Lippmann electrometer where we have an asymmetrical insulation, current flowing in one direction only below 1.2 volts.

For several solutions we have measured the residual current by running the current through a resistance box in series with the cell, and measuring the electromotive force across this box by the usual compensation method, using as a zero instrument a delicate galvanometer. Knowing the resistance and electromotive force, the current is easily found.[3]

[1] We give for convenient reference the coefficients of solubility in water of a few gases at 10° C. and 760 mm.

O_2	0.03852
H_2	0.01944
N_2	0.01918
Air	0.01953
Cl_2	2.585

Ozone is more soluble than oxygen. These values are taken from Table 138, page 125, Smithsonian Physical Tables, Vol. 35 (1897). As we shall show later on, hydrogen peroxide in water has an effect similar to that of dissolved gases.

[2] J. Phys. Chem., 6, 603 (1902).

[3] Mr. W. R. Mott will shortly publish the details of this method and some of its applications.

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In Table IV we have given a few typical points from a number of electromotive force-current curves at low voltages. These curves appear to be of a logarithmic nature. The currents are approximately of the same order of magnitude in different solutions as would follow if the solubility of the gas in the solution were not greatly affected by the presence of other solutes. One striking exception is hydriodic acid containing free iodine where the residual current is over ten times, or 1000 per cent., greater than in hydriodic acid solution alone. This phenomenon can be explained upon the same basis as other residual currents by substituting iodine in place of dissolved oxygen. With this exception it appears that the form of the electromotive force-current curve for residual currents, and the magnitude of the current, does not enable prediction as to what particular ingredient of the solution is being subjected to electrolysis.

TABLE IV.

	V.	A.
nHCl + nZnSO$_4$	0.6	0.000042
nHI	0.47	0.000033
nHI + I (free)	0.36	0.00045
nKCN	0.64	0.0000375
nKCN + nZnSO$_4$ (redissolved)	1.17	0.000033
	1.31	0.000069
	1.26	0.000024
nKCNO	0.37	0.000030
nKCNS	0.53	0.0000495
nKyFe(CN)$_6$	0.14	0.000060
	0.28	0.00012
	0.4	0.00020
	0.56	0.00024
$n/30$ K_2CrO_4	0.37	0.0000030
	0.50	0.0000129
$n/30$ $KMnO_4$	0.41	0.0000090
	0.61	0.000039
	0.77	0.000125
	0.90	0.00021
	1.05	0.00045
	1.16	0.00085
	1.31	0.001686
	1.55	0.0045
	1.91	0.01092
	2.00	0.011
	2.50	0.021
	3.00	0.032
	3.50	0.041
	4.50	0.041

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(2) Large residual currents. We give now the history of the observation of residual currents 100 to 1000 times as large as any yet described in the literature (as far as we have been able to ascertain). We noted for solutions containing salts of iron that continuous currents as large as 10 to 30 milliamperes, corresponding to a current density of 3 to 10 milliamperes per square centimeter, pass much below 1 volt. Having observed this phenomenon in our $FeSO_4$ solution and all mixtures containing it, we conceived the idea that simultaneous oxidation and reduction takes place in such a manner as to allow the current to pass. We then observed that in diluting normal $FeSO_4$ with normal $ZnSO_4$ this current at 1 volt was greatly decreased (see Curves 6 and 7, Plate II), and in those solutions containing $FeSO_4$, which had been allowed to stand uncorked, we noted that the current at 1 volt was even greater than in solutions containing $FeSO_4$ alone, although less than one-fifth the amount of iron salt was present as compared with that in Curve 6 (for $FeSO_4$ alone).

This suggested the idea that ferrous and ferric salt together were conducive to passage of current at low voltages. To confirm this idea, we made up a solution of $FeCl_3$ together with $FeSO_4.(NH_4)_2SO_4$ as stated in the notes on Curve 8. We found that with low voltage—as we had surmised—a very considerable current passed, approximately ten times as great as in the other iron solutions, and with the Curve 8*a* produced it appears that the current starts at zero voltage. This phenomenon has important bearing upon the use of iron salts, especially ferric, in electrolysis.

Since there is no reason to question Faraday's Law, simultaneous oxidation and reduction at the anode and cathode respectively allows current to pass and be wasted. Exhaustion of ferric salt around the cathode and of ferrous salt around the anode is prevented by diffusion. Ferric salts are therefore poor and inefficient electrolytes for plating or other purposes since ferrous salt will quickly be formed, and, as we have shown, the mixture conducts the current without performing useful work. In the use of ferrous salts for plating, at the anode the acid radicle should dissolve away the iron instead of oxidizing the ferrous salt to ferric, and thus producing the mixture which conducts below the decomposition point.

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We consider these large residual currents, observed in the case of iron salts, to be due to the simultaneous oxidation and reduction at anode and cathode. The iron salts are not decomposed because the decomposition points of all iron salts, ferrous and ferric, are above 1.7 volts. The energy is expended in heating the solution and in causing the diffusion of the ferric salt from the anode, where it is formed and is in excess, to the cathode, where it is reduced to ferrous salt. Then we have excess of ferrous salt at the cathode; from here it diffuses back to the cathode and the process is repeated.

Mr. Hill has kindly given us permission to refer to some unpublished data of his. In electrolytic experiments with iron salts, namely, ferric chloride and ferric sulphate in aqueous solution, he found by careful weighing that both the iron anode and the iron cathode lost in weight in every case. The solution of iron observed by Mr. Hill at the cathode is due to the tendency of metallic iron to reduce ferric salts and thus go into solution; the anode corrosion is, of course, the normal phenomenon.

In trying to plate iron out of an iron solution (as is well known) it is desirable to keep all of the iron in the ferrous condition. In 1902 one of us,[1] together with A. B. Marvin, succeeded in getting a smooth coat of iron which stood buffing remarkably well. This coat was secured by maintaining the iron in the ferrous condition by adding methyl alcohol, which acted as an efficient reducing agent. Some other reducing agents which should prove effective are acetone, sugars, sorghum, etc. Organic compounds containing the aldehyde group are especially effective for this purpose.

It is not unlikely that the successful deposition of iron and similar metals from their organic salts, such as oxalates, citrates and the like, is due to the effective reducing action of these acids when decomposed at the anode.

This same precaution should be taken with zinc-plating solutions which contain iron, lest the iron become partly oxidized to ferric condition and cause waste of current.[2]

[1] H. E. Patten.

[2] This idea of keeping iron in plating solutions in the ferrous condition is of considerable commercial importance. A German patent for plating zinc upon iron makes use of this principle, in that grape-sugar is used as the reducing agent. This process is in use at the Brooklyn Navy Yard. In plating metals upon iron, steels, etc., it is important that the iron dissolved from the surface to be plated upon should be kept in the ferrous condition.

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The general principle may be laid down that in electrolyzing, the highest current efficiency will be maintained by avoiding the simultaneous presence in solution of one metal in two or more stages of oxidation. Another phase of this principle is where we have present in solution an oxidizing and a reducing agent which do not react upon each other.

A phenomenon similar to the above and to be explained upon the same general basis is the electrolysis of hydrogen peroxide. The heat of formation of H_2O_2 is +45.2 large calories; far below that of water, 68.4 large calories. Consequently it decomposes into water and oxygen with liberation of energy. This decomposition of H_2O_2 goes on at ordinary temperatures; in contact with the platinum electrodes of our cell a vigorous evolution of oxygen was observed before an electromotive force was impressed upon the cell. As Curve 16, Plate II, shows, there is no polarization value—*i. e.*, counter electromotive force due to chemical change—which indicates that it is possible to have an electrolyte with no decomposition point. The H_2O_2 gave no tilt to the CR line, although a large amount of gas was liberated on electrolyzing. Consequently we ascribe the conductivity observed to the excess of acid present in the commercial H_2O_2 used, whence we deduce the idea that even below their decomposition points electrolytes assist in conduction.

In electrolyzing H_2O_2 we may conceive of an oxygen atom going to one electrode and a water molecule going to the other. This would require no external energy since H_2O_2 decomposes of itself into H_2O and oxygen with liberation of energy. Another aspect of this reaction considers the H_2O_2 as decomposed into H_2 and O. When the hydrogen is liberated on the cathode it combines with the oxygen from the H_2O_2 with liberation of energy equal to that required for the decomposition of water.

B. Conduction:

The idea of conduction below the decomposition point is old. The fact that residual currents flow, had to be explained, of course, by assuming conduction by the solution below the decomposition point. As to whether the quantitative conductivity of the various salts present in the solution remained the same, most of the literature on the subject shows that there is only a hazy notion as to the exact condition of this conduction. Some have given evidence

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that they believed the quantitative conductivity of the solution to be the same above and below the decomposition point. A clear-cut statement of this is found in an article by P. Weightman[1] where he says that, "although the conduction through the solution takes place by all the ions present, the copper will be deposited far more easily than the zinc; and in fact the zinc will not be deposited at all until a very large difference in the concentration of the copper and zinc 'ions' is reached."

In our curves for the mixtures the CR line of the upper branch is practically parallel to the CR line of the lower branches, showing that all the salts in the solution share in the conduction (not in the electrolytic deposition or reactions) above and below their respective decomposition points.[2] The fraction of the total conductivity of the solution due to each salt, is the same above and below the decomposition point of that salt.

Examples showing that the lower branches of the curves are practically parallel to the other branches are curves of such mixtures as $CdSO_4$ and $ZnSO_4$, $CuSO_4$ and $ZnSO_4$, etc. An example where we have greater conduction is the mixture of ferric chloride and ferrous ammonium sulphate, where the lower branch is nearly horizontal (as would be expected) as well as the upper branch to which it is parallel.

The interesting experiments of Richards and Landis[3] show that 0.1 per cent. sulphuric acid electrolyzed in a very long tube gives a CR line, which starts from zero voltage, following Ohm's Law.

The explanation advanced by them was that the extremely small current, allowed to pass because of the great resistance of the electrolytic cell, was easily completely depolarized by the dissolved gases. Their explanation agrees with the ideas and experiments conceived and performed by us with regard to large residual currents in mixtures of ferrous and ferric salts and in

[1] Trans. Am. Electrochem. Soc., 2, 56 (1902).

[2] As numerous investigators have maintained (Cf. "Influence of the Solvent in Electrolytic Conduction," J. Phys. Chem., 6, Nov., 1902, and bibliography given there) a solution is to be considered as a union of solvent with solute. There is no criterion by which we may discriminate solvent from solute in the homogeneous substance called a solution. For instance, in a solution consisting of alcohol and water, we may as well consider the water to be dissolved in the alcohol, as to hold the ordinary conception that the alcohol is dissolved in the water. The discrimination, then, between solvent and solute in considering the physical properties of a solution is a mere convention. These properties are dependent upon the chemical nature of the combination formed from solvent and solute (cf. T. C. Fitzpatrick: Phil. Mag., 24, 377 (1887).

[3] Trans. American Electrochemical Society, 3, 105 (1903).

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hydrogen peroxide. The H_2O_2 curve is an exact parallel to their curve except that we had a current a thousand to a million times as large, completely depolarized by the H_2O_2.[1]

Summary of the points to be observed in securing perfect depolarization at both electrodes and therefore CR curves starting from zero voltage:

(1) Increase the quantity of the depolarizing material such as dissolved gases, H_2O_2, mixtures of oxidizing and reducing agents which do not react upon each other, as ferrous and ferric salts.

(2) Decrease the current density by, (*a*) increasing the area of the electrodes; (*b*) increasing the resistance of the cell; this may be done by increasing the distance between the electrodes, and by decreasing the cross section of the conducting liquid.

Products of electrolysis do not give a criterion as to which substances share in the conduction. Consequently it would seem that a charge of electricity must be transferred from one substance to another in the process of electrolysis. In other words, the energy carried by one may be used by the other, and therefore transferred to it and used in doing chemical work. The nature of the products which separate out on electrolysis do not enable us to decide to what extent, if at all, the solvent enters into the conduction.

C. Decomposition:

In the case of all mixtures containing iron salts, of which we have given 6 curves, it is found that they have three or four characteristic points of inflection in common. In mixtures of $CdSO_4$ and $ZnSO_4$, of K_2SO_4 and $ZnSO_4$, of H_2SO_4 and $ZnSO_4$, of $CuSO_4$ and $ZnSO_4$, we have for the lower decomposition point practically the decomposition point which would be given by the solution of the salt alone with no $ZnSO_4$ present. We use the term decomposition point here in the sense that it is the intersection of the CR line with the axis of ordinates. On this lower branch of the curves the CR line is practically parallel with the CR line of the upper branch, showing that while the $ZnSO_4$ is not being plated out it takes part in the conduction; otherwise the CR line would be tilted toward the axis of ordinates due to change in resistance. The voltage of decompo

the American Electrochemical Society.[3] Kahlenberg pointed out

[1] The question might arise, why not consider H_2O_2 to be present, and to do the depolarizing in place of dissolved gases for small residual currents in aqueous solutions.

[1] Bose: Ztschr. für Elektrochem., Oct. 6, 1898.

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its intersection with the axis of ordinates in mixtures of $ZnSO_4$ with $CdSO_4$, $FeSO_4$, H_2SO_4, $MgSO_4$ and K_2SO_4 approximates 2.8 volts in each case. An exception to a generalization which might be made on this basis is the mixture $CuSO_4$ and $ZnSO_4$, for which the upper decomposition voltage falls at 2.2. In seeking an explanation for this exception we are led to consider the deposition of alloys from aqueous electrolytes.

The electromotive force furnished by a cell consisting of zinc and copper against zinc[1] is at 69 molecular per cent. of zinc 0.005 volt, and from 69 to 66 molecular per cent. (Zn_2Cu) there is an abrupt rise to 0.700 volt. From there on the curve is less steep, decreasing to the value 1.13 volts for copper against zinc. At the percentage Zn_2Cu, that is, 66 molecular per cent. of zinc, the heat of formation of the alloy is a maximum and positive (heat given off in forming). The current density at which an alloy of copper and zinc plates out of a mixture of their sulphates (saturated)[2] is given as,

Cur. per sq. cm.	Cu. Per cent.	Zn. Per cent.
0.008	100	0
0.200	94	6
0.580	92	8

According to this table, after getting up to 6 per cent. of zinc, very little change is made in the per cent. of zinc by greatly increasing the current density. If with the saturated solution of $ZnSO_4$ and $CuSO_4$ the per cent. of zinc plated out did not exceed 8 in the above instance, the probability is that our alloy obtained at the break in Curve 13, Plate II, contained by no means so high a percentage of zinc.

The increase in voltage required to plate out an alloy of zinc and copper should be the voltage required for copper plus the electromotive force that would be furnished by a cell of copper against the alloy. In the table already given this would amount to 1.13 volts —0.700 volt or 0.43 volt. Taken from Curve 13, Plate II, and from Table III, the lower polarization voltage of decomposition for $CuSO_4$ mixed with $ZnSO_4$ is 1.70 volt; and the upper similar value, due to the alloy plating out, is 2.20 volts. The difference between these is 0.50 volt. Comparing this 0.50 volt with the 0.43 volt we see that the effect is due to the plating out of

[1] Herschowitsch: Ztschr. phys. Chem., 27, 123-126 (1898).
[2] Sutton: Elec. Power.

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the alloy which gives considerably less voltage when used in a cell against zinc than most alloys of zinc do. This difference of voltage is, as already given, 0.700 volt. The decomposition point given where zinc alone is plated out is, according to Table III, as a general average about 0.60 volt higher than where this alloy is plating out—as indicated by the abrupt curvature of Curve 13, Plate II.

Alloys of zinc with a more electro-negative element as a rule furnish very nearly the same potential as pure zinc alone even where the per cent. of zinc is very small, even as low as 3 or 4 per cent. As examples of this, may be cited the alloys zinc-cadmium, zinc-bismuth, zinc-tin and amalgams of zinc. From this we see that a very small per cent. of zinc plating out will cause a rapid increase in the required electromotive force of plating. This explains the almost vertical rise that occurs in the curve for the zinc sulphate and cadmium sulphate, Curve 5, Plate II.

These alloys have a negative heat of formation and therefore require energy for their formation, and require a higher electromotive force than might otherwise be expected to plate them out. (The greater readiness with which zinc-copper alloy plates out of cyanide solution, is due to the nearly equal value for the heat of formation of copper cyanide and of zinc cyanide.)[1]

D. Relation of the Caspari Phenomenon to the Plating-out of Zinc:

The general law, as given in many places in the literature, is that those "ions"[2] leave the solution which demand for their liberation the least consumption of work. Upon this basis, which we have no desire to call in question, why should zinc sulphate decompose at a voltage of 2.35 (the point where the metallic zinc first appears) in aqueous solution where in the case of acid and basic solutions water is decomposed at a voltage of 1.70 volts between platinum electrodes? The general relative magnitude of these two values is substantially corroborated by data on their heats of formation. A phenomenon investigated by Caspari[3] shows that certain "excess electromotive force" is required to plate out hydrogen on certain metals from a hydrogen anode.

[1] Herschowitsch: Ztschr. phys. Chem., 27, 123 to 166 (1898).
[2] Used in Faraday's sense.
[3] Ztschr. Elektrochemie, 6, 37-41 (1899).

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	Volt.		Volt.
Pt (platinized)	0.005	Sn	0.53
Au	0.22	Pb	0.64
Pt (ordinary)	0.09	Zn	0.70
Ag	0.15	Hg	0.78
Cu	0.23		
Pd	0.48	Amalgams act like mercury.	

This series shows not the slightest relation to the electrochemical series of the metals. This excess electromotive force added to the decomposition point of water gives a decomposition voltage, where we use platinum anode and zinc cathode, to prevent hydrogen coming off until the electromotive force is equal to 2.40 which is above the decomposition point of zinc sulphate.

The excess electromotive force for hydrogen coming out upon platinum alone is 0.09 volt. This added to 1.70 volt, the decomposition voltage of water gives only 1.79 volts; consequently, the question may be raised, where does the excess voltage necessary to give 2.35, the decomposition voltage of $ZnSO_4$, come from? If we apply Helmholtz' conception of the thin layer coming out upon the electrode before the voltage of decomposition is reached, to the plating-out of zinc, it is seen that an attempt to plate out hydrogen (from a hydrogen anode) upon such a thin layer of zinc would require 0.70 volt above the 1.7 volts necessary to decompose water. As was stated above, this gives 2.4 volts as the decomposition point of water between platinum and zinc electrodes, and as $ZnSO_4$ requires only 2.35 volts to decompose it, the zinc plates out.

We have determined current-electromotive force curves for all the solutions in which single potentials of zinc are given: halogen salts, cyanide compounds, nitrogen compounds, salts of selected oxygen acids, and their mixtures with zinc sulphate. These will be published later.

We desire to thank Prof. C. F. Burgess for placing at our disposal a private laboratory, current, instruments and his card catalogue, and for assisting us with all the means at his command in carrying out our ideas. The connection of one of us[1] with the chemical department of this university has also greatly facilitated our work.

[1] H. E. Patten.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

ELECTROLYTIC CONDUCTION WITHOUT ELECTRODES.

By A. B. Marvin.

When a metallic conductor is moved across a magnetic field, an electrical potential is developed in the conductor as the result of this motion. If an electrical circuit includes the conductor, a current will flow because of this pressure. The exact molecular means by which the current is transmitted through the conductor cannot readily be determined, but for convenience in reasoning is supposed to consist in some sort of vibration or stress in the conductor or in the surrounding medium.

The question has arisen as to whether a pressure would likewise be generated in a tube of electrolyte by moving it across a magnetic field; and further, whether a current would flow in the electrolyte due to this pressure provided the electrolytic circuit was short-circuited on itself to form one continuous path of electrolyte with no electrode of any sort interposed.

From the standpoint of electrical practice, it seems probable that such a tube of electrolyte would be acted upon in the same way as a wire, except of course that there would be a difference in current output proportional to the difference in resistance in the two circuits. From the standpoint of physical chemistry the results of such an experiment are not so obvious. The suppositions of the generally accepted ionic theory seem to throw some doubt on the effects which might be presumed to result. Thus if the electrolytic circuit be considered as made up of a great number of distinct particles or ions, each carrying an electrostatic charge, either positive or negative, it is not altogether clear how by moving the electrolyte across a magnetic field the ions will be sorted out and the positive ions sent one way and the negative the other. The usual assumption that the ions move because of the electrostatic attraction and repulsion of the electrodes does not hold because there are in this case no electrodes at all. Without electrodes, the charged ions would have no definite place to unload their charges

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and likewise no means of discharging except possibly by neutralization of ions of unlike polarity.

The assumption could of course be made that the ions remain charged with their respective polarities and circulate through the closed circle of electrolyte, those of the plus kind going around the circuit one way and those of the minus sign around the other, the movements being possibly in concentric circles. The reason for such an assumption is, however, not obvious.

While the question appears to appertain more to the theoretical than to the practical, a brief description of a few experiments made some time ago in the laboratory of applied electrochemistry of the University of Wisconsin may be of interest.

The objects of the experiments were to determine quantitatively if it is actually possible to pass a current through an electrolyte without the use of electrodes of any sort, either for introducing the current or for detecting its flow and whether the conduction, if it does occur, is in any way different from that which occurs in a metallic conductor under like conditions.

At first thought, it did not appear altogether impossible to convert a direct current dynamo into an electrolytic dynamo by substituting tubes of electrolyte for the copper wires in the armature slots, using a commutator of peculiar construction. A few calculations as to the efficiency of such a machine bring out very strikingly the enormous difference in the resistance of copper and of even the best of aqueous electrolytes. A machine of this type built on ordinary lines of dynamo construction would yield a current of only a few millionths of an ampere, even when on short circuit, because of the great internal resistance of the armature winding itself.

The type of dynamo commonly called unipolar, and in which the magnetic flux of but a single pole is used, appeared to present some advantageous features; first because of the absence of a commutator and second because the moving conductors could be made short and thick, and hence of low resistance.

A typical form of unipolar dynamo is shown in Fig. 1 in which N is a permanent magnet, B the movable or generating conductor, and C D mercury cups, into which the moving conductor dips and by aid of which, electrical connection is made with external circuit. Since the magnetic flux is of the same sign at all

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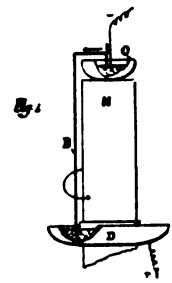
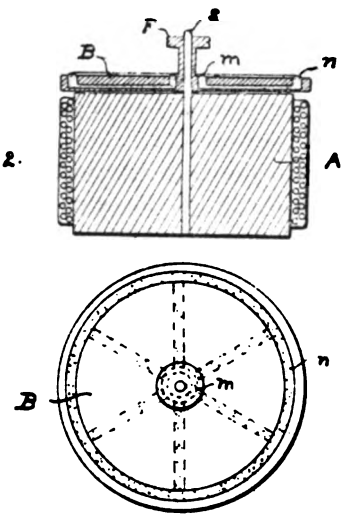
points about the pole, the pressure generated in the conductor as it revolves about the pole will remain continually in the same direction, and hence the necessity for a commuter does not arise.



An apparatus operating on this principle but with an electrolytic conductor substituted for the metallic conductor was constructed as shown in Fig. 2. It consisted essentially of an electromagnet *A* of approximately 200 turns, wound on a soft iron core 12 centimeters in diameter. Through the center of the core projected a shaft *S* on which the armature or moving conductor was rotated.

The armature consisted of a wooden block *B* in which radial channels had been chiseled out. These channels, when filled with electrolyte, were to serve as conductors in the same way as the wire *B* of Fig. 1, the advantage of a plurality of slots over a single slot being a decrease in the internal resistance. This armature was adapted to seat on the shaft *S* and to be revolved by means of the pulley *F*. Two annular channels, *m*, *n*, were provided to serve as slip rings from which the current could be led off from the moving part through rubber tubes to a suitable measuring instrument. To prevent the solution from flying out because of centrifugal action, the channels and rings were tightly filled with wicking, connection being made with the external circuit by wet cloth brushes bearing on the wicking in the channels.

Fig. 2.



The external or instrument circuit consisted of a solenoid of glass tubing filled with the electrolyte, the solenoid serving as the coil of a galvanometer.

It was found when the armature was set in motion that only a very low speed could be maintained because of the tendency of the solution to fly out. Various expedients were tried to keep the

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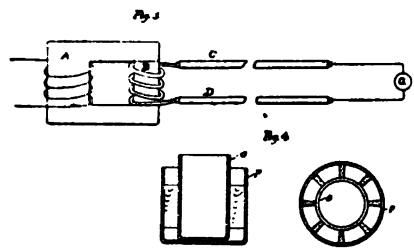
radial channels filled with solution, but it was found impossible to maintain any reasonable speed for the armature and at the same time keep the electrical circuit continuous in the radial channels. At low speeds the pressure generated was entirely too small to be detected by the magnetic action of the current flowing through the glass solenoid, and hence in that respect the experiment was a failure.

It was found, however, that by inserting two small copper wires through the rubber tubes which led from the slip rings to the solenoid, and using these as voltmeter leads to connect to a galvanometer, a pressure was readily detected when the armature was set in motion. The pressure increased with the speed up to the point where the circuit opened from centrifugal action on the solution. The solution in this case was saturated copper sulphate and so no chemical or polarization effects on the copper terminals enter as factors in the experiment.

The same general results were verified by an arrangement such as is shown in Fig. 3. *A* was an electromagnet of approximately 200 turns and capable of carrying 50 amperes momentarily. *B* an iron core, over which was slipped a glass solenoid containing the copper sulphate solution. Connected to the terminals of the solenoid were two glass tubes *C*. *D*, 2 meters long and 5 centimeters in diameter. Through the corked ends of these tubes were inserted the two copper voltmeter terminals which in turn led to a galvanometer.

By opening or closing the circuit of electromagnet *A*, a magnetic flux was caused to cut the glass solenoid of electrolyte and so set up a pressure which was transmitted through the tubes *C D* to the galvanometer. The object in using the long tube *C D* was to remove the galvanometer and its parts from the sphere of magnetic influence of the electromagnet *A*. Proper tests were made to see that the galvanometer was so protected from stray fields.



Thus far in the work it had been found impossible to detect the current induced in the electrolyte without the use of metallic test electrodes.

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It was thought that some of the principles commonly employed in a three-phase induction motor might offer a means of detecting the current flow without the intervention of electrodes. To this end a rotor was built up, as shown in Fig. 4, by placing one glass jar within another and separating the two by wooden strips, the strips being short enough to allow a space at either end to connect one vertical channel electrically with the next.

The space between the jars and wooden strips thus corresponded in form to the copper conductors usually employed in a squirrel cage rotor for induction motors.

The space between the jars was then filled with a 25 per cent. sodium hydroxide solution, the solution thus taking the place of the copper conductors.

A three horse-power, three-phase induction motor was then divested of its bearings and its rotor and turned over on its side so that the jar of solution could be suspended from a torsion head into the space normally occupied by the rotor. It was believed that the excitation of the stator would induce eddy currents in the electrolyte which by reaction would cause the jar to turn on the torsion head, the amount of displacement of the head bearing a definite relation to the conductivity of the solution within the jar and so furnishing a means of obtaining comparative resistance measurements without the use of electrodes. However, when the current was put on, the jar showed no tendency to turn. Owing to the weight of the jar and its solution the suspension could not be made delicate and whatever tendency toward rotation did exist was no doubt taken up by the resistance of the suspension. That there was a tendency to rotate was shown by the fact that the solution near the top of the jar began slowly to turn in the direction of the rotary magnetic field of the stator. In order to better observe this phenomenon the inner jar and the wooden spacers were slipped out and the outer jar completely filled with solution. Upon again completing the circuit to the stator, the solution started slowly around in the direction of rotation of the field, and upon reversal of two of the three leads to the stator thus reversing the phase rotation of the field, the solution gradually came to rest and then started up in the opposite direction. This undoubtedly shows the presence of local currents in the body of electrolyte which by reaction on the field of the stator drew the solution around with the moving field.

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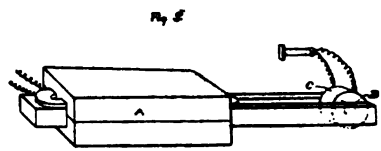
By properly designing the rotary field, this torsion effect could probably be greatly increased, and although a method of determining resistances in accordance with this principle does not appear altogether convenient, in certain special cases it might be of value.

Another experiment was tried in which the results were rather more positive than in any of those just described.

The apparatus consisted essentially of two alternating current transformers of somewhat peculiar construction. The primary of the first was excited from a 125 cycle alternating current power circuit. Its secondary winding, which consisted of a tube of electrolyte, served also as the primary of the second transformer, and the secondary of this second transformer was connected to a telephone receiver.

Thus the impulses induced in the core of the first transformer were transmitted through the electrolyte to the core of the second and thence to the telephone.

In detail the apparatus was arranged as shown in Fig.5. The primary of transformer *A* consisted of twenty-three turns of copper wire and the secondary of one turn of electrolyte contained in a thin wooden trough. The transformer core was of the shell type, the inner tongue being 6 x 18.5 centimeters and the outer ones 5.3 x 18.5 centimeters. The wooden trough was 5.3 x 3 centimeters where it passed around the core but was 5.3 x 9.5 centimeters beyond the core where the space available allowed this increase in area. The trough was built up of dry pine, the parts being wedged together to avoid the use of nails which might accidentally come in contact with the electrolyte. After the box was built up it was boiled in paraffine to make it water-proof.



The extremities of this trough were run out beyond the sphere of magnetic leakage from the transformer and connected by a glass tube *B* which passed through the two branches of the wooden trough and also, with a snug fit, through a test coil *C* built up like an ordinary Gramme ring. The core of the ring consisted of iron wire, shellaced before winding, and over this core was wound 700 turns of No. 30 insulated copper wire which, in turn, was connected to a telephone receiver.

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With the arrangement described, an alternating impulse impressed on the copper winding of transformer *A* would induce an impulse in the electrolytic secondary, and if an electrolyte is capable of transmitting a current under such circumstances, the current which would be caused to flow through the glass tube would throw out lines of force which by cutting back and forth through the inner halves of the 700 turns of copper wire would cause a humming of the telephone.

With the apparatus as described but with no solution in the trough an alternating pressure of 190 volts was impressed on the primary of transformer *A*, through which a magnetizing current of 50 amperes flowed as the result. The magnetic density in the laminated core was so great and the noise resulting therefrom so loud that it was found necessary to run the telephone leads to a distant part of the building and so remove the telephone from the disturbing influence of this noise. With the telephone so situated, it was found that a continuous humming was noticeable as the result of the magnetic leakage or stray field which spread through the air from transformer *A* to the small test transformer. Various methods of magnetic shielding were attempted but with little success so that this element was present throughout all the subsequent tests.

With the power circuit connected to transformer *A* and an assistant listening attentively at the telephone, the electrolyte was slowly poured into the wooden trough. As it rose to the level of the glass tube and so connected the two arms of the trough the humming in the telephone changed to a loud noise, thus showing the transmission of current through the continuous circuit of electrolyte.

Rubber stoppers were fitted to the ends of the glass tube and could be inserted or withdrawn by the aid of glass handles, thus alternately opening and closing the electrolytic circuit. In this manner signals such as the Morse letters could be readily transmitted to the observer at the telephone by merely inserting and pulling the stoppers at proper intervals.

The electrolyte used was a 25 per cent. solution of potassium hydroxide and the electrolytic circuit presented a total resistance of approximately 30 ohms as determined by measurements distinct from the above experiment. Preliminary tests showed that the

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small or test transformer and telephone were sensitive enough to detect a current of 0.01 of an ampere in the glass tube of electrolyte, provided no disturbing influence such as a stray field was present. With a stray field the sensitiveness was much less, for then it became necessary to detect a change in the volume of the sound instead of determining the difference between silence and sound.

After the experiment had been completed, the trough was replaced by one turn of copper wire and an observation made of the voltage induced in this wire, so that some idea could be gained of the voltage which had been formerly induced in the electrolyte. With the same pressure and current on the main transformer as before, *viz.*, 190 volts and 50 amperes, the single turn of wire showed a pressure of approximately 3 volts. Since there were but 23 turns to the primary, the volts per turn, with 190 volts total pressure, would be a little more than 8 volts. Theoretically this would mean 8 volts on the single turn of the secondary; but practically, the extreme magnetic density and consequent leakage reduced it to only 3 volts.

The apparatus was capable of detecting pressure less than 3 volts, but was not sensitive to values below 2 volts. At this latter value the variations of sound in the telephone caused by moving the rubber stoppers were completely lost in the ever-present field of disturbance

When a copper wire of 30 ohms resistance was substituted for the solution in the trough the variations in the telephone again disappeared at the same voltage as when the solution was used. If then there is a difference in the two classes of conductors when acted upon by induction this difference is too slight to be detected by the apparatus used in this experiment.

No electrolytic changes, such as the formation of gases or other electrolytic products, could be detected.

These experiments show then, that it is possible to generate currents in electrolytes solely by induction, and of such magnitude that they may be detected by their magnetic effect alone, without the use of electrodes of any kind. Whether decomposition takes place is not definitely determined, but probably it does not.

It should be noted here that aside from resistance measurements, the principle of inducing currents in electrolytic circuits

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might be used to advantage in such apparatus as Nernst lamps where difficulties are encountered with the terminals or electrodes. Thus each lamp might possibly be made up as a miniature transformer of which the primary or power circuit is metallic and of which the secondary is a glower arranged as a ring or spiral, short-circuited on itself.

The practical difficulties of such an arrangement would be great, for the glower material has not only a high resistance, which would necessitate several turns to secure the necessary voltage, but also is of such a nature that it cannot easily be formed into a winding.

This same principle of inducing the current in the light-giving body might possibly be applied to mercury vapor lamps and so furnish a means for overcoming some of the difficulties now present in such lamps. Thus it does not appear impossible to construct a vapor lamp in which the light-emitting tube is a coil of glass tubing filled with mercury vapor and short-circuited on itself. With such an arrangement there would be no necessity for electrodes, except possibly to start the arc, and hence no rectifying or insulating action when alternating currents flow. It is possible that the arc might be established or assisted by carbon or metal filaments threading the tube or by some arrangement of a similar nature.

While these suggestions may or may not be practical, nevertheless, the fact remains that it is possible to induce currents in electrolytes and to detect their flow without the use of electrodes of any kind.

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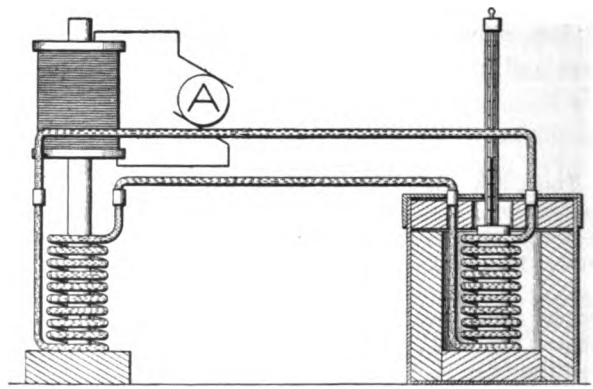
DISCUSSION.

MR. CARL HERING: Mr. President, this paper has interested me very much, as it seems to me to be probably the first real demonstration of electrolytic conduction without electrodes. It is, of course, to be regretted that an alternating current had to be resorted to to demonstrate that, as it would have been still more interesting to have shown electrolytic conduction with a continuous current, but this involved very great difficulties; I suggested an apparatus for doing this in my paper to which Mr. Marvin referred, but it would be rather difficult to carry out. While referring to my former paper, I would like to take the opportunity to make a correction. In that paper I referred to certain of the experiments just described by Mr. Marvin but attributed them to Dr. Kahlenberg, because he had told me about them. It seems now, however, that I should have attributed them to Mr. Marvin.

DR. W. D. BANCROFT: These experiments, while very interesting, can hardly be called new, because this principle was demonstrated experimentally by Guthrie and Boys in England, some twenty years ago, and published in the *Philosophical Magazine*, (5) 10, 328 (1880).

DR. N. M. HOPKINS: This is a matter of great interest. About two years ago I succeeded in showing conduction without electrodes, and if it is in order I will sketch the apparatus employed, on



the black board. This apparatus was designed and set up in the laboratories of the Columbian University in Washington. I had two spirals made of glass tubing which were connected with glass

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tubing, with rubber connectors. This system was filled with a dilute sulphuric acid electrolyte. In the center of the spiral on the left I placed a soft iron bar wrapped with a conductor of the first class, leading to and connected with a small alternating current generator placed at a distance. This coil of electrolyte was placed in a calorimeter, as indicated, with a thick felt lining as shown, and in the center of this spiral was suspended a small cylinder of thin soft iron. In the center of this little iron cylinder was placed a Beckmann thermometer adjusted to indicate at the temperature of the laboratory, and when things had settled down to a constant temperature a reading was taken. The alternator was next started and the thermometer watched. There was almost immediately a rise of temperature due to the heating of the little iron cylinder by hysteresis from the alternating current passing through the spiral containing the electrolyte. Each time the cylinder was raised a little out of the position of maximum excitation the mercury column in the thermometer would fall, and each time it was lowered the mercury would rise, indicating that we had a current flowing through the electrolyte.

PROF. C. F. BURGESS: Would there be any heating if the glass tube had been cut in any part of the circuit; that is, if your electrolyte circuit had not been complete, would there not have been just as much heating in the iron core surrounded by the electrolyte? What I am referring to is the stray field which is set up by the magnet magnetized by the metallic conductor carrying an alternating current. If another iron core is placed in such stray field there is liable to be a certain amount of heating. In one of the experiments to which Mr. Marvin refers, he got the same effect even with the cores very widely separated, the induced magnetism being detected not by thermal means, but by using a telephone receiver.

DR. HOPKINS: The apparatus was not tried with the tubes empty. I may say, however, that the two spirals were about a meter apart, and the calorimeter, I would state, afforded a fair protection, but I do not know that there may not have been a stray field there as you suggest, but I doubt its ability to affect matters considering the manner in which the apparatus was operated. It would, of course, be of interest to break the continuity of the electrolyte during such an experiment, thus eliminating any possible

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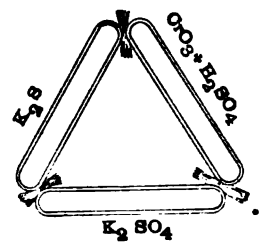
question as to the presence within the calorimeter of a stray field.

MR. HERING: Instead of the thermometer it might have been better to have wrapped a wire around an iron core and put it into the secondary coil, connecting the wire to a telephone; then if a sound was heard in the telephone, it would have shown that the current had been led from one to the other.

DR. H. S. CARHART: This is a better magnetic circuit at the left and that favors, of course, the stray field, too. It seems to me that the only way to check that is suggested by the question of Mr. Burgess, *viz.*, to determine whether there is any heating effect produced in the calorimeter when the liquid circuit is entirely open.

MR. REED: This subject is very interesting to me. I am not familiar with the work of Boys which Dr. Bancroft has referred to. Some time ago I tried to determine whether there was any possibilty of establishing a direct current through a circuit consisting entirely of electrolytes, but I failed to get the slightest indication. My experiment was a very simple one. I joined in the form of a triangle three flat porous cups, as shown in this sketch.



The electrolytic circuit was completed at the edges of the cups with blotting paper soaked in the corresponding solutions. A U-shaped mass of laminated iron was inserted in the electrolytic triangle. On one arm of the U was a coil of fine insulated wire connected to a very delicate D'Arsonval galvanometer. On opening and closing the electrolytic circuit there was no distinguishable movement of the needle. But when an electrode of carbon or platinum was used in place of one of the pieces of blotting paper a strong deflection was produced.

MR. W. L. SMITH: One thing that occurs to me in connection with this apparatus of Mr. Marvin's is a possible electrostatic influence. Has it great enough length of copper sulphate solution

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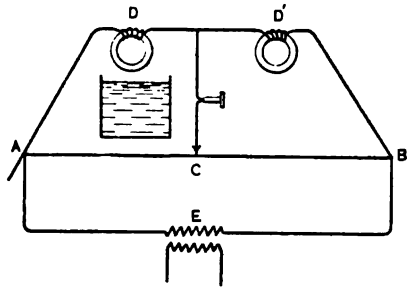
conductor? Isn't there a possibility of electrostatic disturbance that might account to some extent for the noise in the telephone?

PROF. BURGESS: I have attempted to use the conductivity of electrolytes without electrodes as a means for measuring resistances, in the manner shown by the accompanying sketch. D and



D' indicate two small continuous iron cores of equal dimensions and wound with an equal number of turns of wire carefully insulated. These two coils were connected in the two arms of the Wheatstone bridge, the other arms consisting of a non-inductive resistance A B. The current was supplied to the system from an alternate current transformer E. By varying the position of C, a balance may be effected, producing no sound in the telephone receiver. It was thought that by lowering one of the coils into the electrolyte, its impedance would be lowered, due to the fact that the electrolyte constitutes a closed circuited secondary and that the balance would thereby be destroyed. By adjusting for another balance, the distance through which the point C moves should be a factor for the determination of the resistance of the electrolyte. No satisfactory results were obtained, however, due to the lack of sensitiveness of the apparatus. Calculation shows the reason for this. The resistance of the electrolyte constituting the closed circuit secondary is in all cases so high that the energy expended in it bears an extremely small ratio to the magnetizing energy. This shows the almost utter impossibility of utilizing the induced pressure without electrodes for passing a current through such a conductor as a Nernst lamp glower or other similar conductors, as suggested by Mr. Marvin. It is possible that with the use of very much higher frequencies than are commonly available, this might be effected.

PRES. RICHARDS: I think that if Mr. Marvin has proved any-

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thing by his paper, he has proved that the title of it is not justified —that instead of proving *electrolytic* conduction without electrodes, he has proved only *metallic* conduction without electrodes, that is, metallic conduction in the sense of being conduction of Faraday's first class; for, in his experiment where he substituted a copper wire of the resistance of 30 ohms for an electrolyte of the resistance of 30 ohms, he was able to observe no difference in the results, or, if there was any, it was too slight to be detected by the apparatus used in his experiment. In other words, he simply proved that his electrolyte with a resistance of 30 ohms acted like a metallic conductor with a resistance of 30 ohms, and that no electrolytic changes, such as the formation of gases, or other electrolytic products, could be detected; so I think he has not proved that the conduction is electrolytic conduction, but that it is, as far as it goes, conduction of the same kind as the conduction through any conductor of known resistance. That fits in with the observation of Mr. Landis and myself, in our experiments, that when the resistance of the electrolyte was high, we obtained a result which showed that the electrolyte acted as a conductor of the first class, within the limits of error of the apparatus which we used; or if there was any deviation from that, it was similarly too slight to be detected by the apparatus used in our experiment. I therefore feel that this work has substantiated the fact that an electrolyte, under certain circumstances, may conduct electricity without (that is, practically without) decomposition, or as a conductor of the first class.

MR. HERING: I differ very decidedly with our president on this point. I do not think that Mr. Marvin's tests show that there is any metallic conduction in the electrolyte at all. The result shows what it is claimed by him to show, and that is all. The conduction which he has shown to exist there is not necessarily any different from the conduction in any electrolyte between electrodes. In other words, the conduction through that circuit is probably of exactly the same nature as though there were electrodes in that circuit somewhere, so that we cannot conclude from these experiments that there is metallic conduction in electrolytes. Furthermore metallic conduction would be in conflict with Faraday's Law, which law accounts for the transportation of all the electricity on the ions, that is, electrochemically, and if there were any metallic

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conduction besides, the part of the current so conducted would not decompose and would therefore not be accounted for electrochemically; but as Faraday's Law accounts for all the current none of it could have been conducted metallically, unless it is so extremely small that it escapes our notice. What I have said, of course, applies to currents which decompose; what kind of conduction there is below the point of decomposition may still be uncertain.

MR. B. MCNUTT: What is there in Mr. Marvin's paper to show what kind of conduction it is? How can one tell from the data he has given us whether it is electrolytic conduction or metallic conduction; in other words, why does Mr. Hering state that it is electrolytic conduction, whereas Dr. Richards states that it is practically metallic conduction or conduction of Faraday's first class.

MR. HERING: I wish to correct something Mr. McNutt said. I did not say that the test does not show the presence of metallic conduction; I simply said that it does not show whether it is metallic or electrolytic.

MR. REED: It seems to me that, while these experiments do not show what takes place in the molecules of the electrolyte, the question raised in Mr. Marvin's paper is a pertinent one. If the conduction is electrolytic in this case, that is, is effected by a movement of ions in two opposite directions, I think it is a pertinent question to be asked,—What is it that causes the movement of these ions? We cannot say that they are drawn towards any electrode, as Mr. Marvin says, or that they are repelled from any electrodes. In other words, this movement of ions cannot be the result of any directive forces to or from any electrode, and that is the theory, as I understand it, of electrolytic dissociation, that the electrolytic conduction is produced in that way, by these charges causing a directive influence on the ions, making them move in specific directions towards electrodes.

PRES. RICHARDS: If I may explain what I meant by using the term metallic conduction, I mean such kind of conduction as occurs in solid metallic conductors, where $C = \frac{V}{R}$.

MR. REED: Where there is no visible decomposition?

PRES. RICHARDS: Without decomposition of the substance through which the current passes, *i. e.*, without electrolysis, for I

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take the term electrolytic to mean "separated by electricity", the etymology of the word meaning that; and by metallic conduction I mean the conducting of a current without separating the constituents of the compound. In Mr. Marvin's experiment there is neither actual nor possible proof that the conduction is electrolytic, while he has for practical purposes, and as far as his experiments go, proved conduction of the metallic kind, and that is all.

MR. REED: Without any changes chemically?

DR. CARHART: This seems to me largely a matter of terms. As far as the discussion has proceeded, judging from the last remarks made by our president, I surely would be unwilling to agree with him, that because we have no separation of the constituents of this electrolyte anywhere in the path of the circuit, it is therefore metallic conduction. We may have the conduction of electricity through that electrolyte without electrodes, possibly without any visible electrolytic dissociation, and yet the actual process of conduction in this case may be totally different from what we have in metallic conductors, where we have no movement of ions, or anything similar to ions. I believe attempts have been made to show that in metallic conduction we have a movement of the particles or ions, and those attempts have utterly failed. I believe we all agree, if it is proved that there is a circulation of alternating currents in this electrolyte, that it in all probability takes place by the movement of the ions in opposite directions, which is not metallic conduction.

DR. BANCROFT: I quite agree with Mr. Carhart. It is a question of definition. If Mr. Richards wishes to introduce his own private definition, he has a right to do so. The usual definition, however, of electrolytic conduction is that the passage of electricity is accompanied by transfer of ponderable matter; and under that definition there is no difficulty. Mr. Richards' definition apparently is, that electrolytic conduction takes place only when there is decomposition.

MR. REED: I take the ground that that is Faraday's definition, as well as Professor Richards'. The derivation of the word is from the very fact that there is a separation, a destruction of the compound by the electric current. Faraday defined an electrolyte as a compound that conducts with decomposition and I supposed that had always been the meaning of the term. This other defi-

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nition is the recent or private definition, *viz.*, "conduction in which ponderable matter is carried." I did not understand Dr. Carhart very plainly when he said that we might not have any electrolytic dissociation at the electrodes. As I understand electrolytic dissociation it has nothing to do with the electrodes. It occurs when a soluble substance is dissolved in a solvent which forms a conducting electrolyte. What takes place at the electrodes when the current passes is something entirely different. The current does not produce electrolytic dissociation but changes ions into atoms or atoms into ions.

MR. HERING: I should like to be clearly understood in this matter. All I meant was this: Suppose there was a long trough with electrodes inserted near the ends; we know there is electrolytic conduction in the liquid in the middle, far removed from either electrode. Now I claim that the liquid at that point conducts in precisely the same way, whether there are electrodes in the ends of the trough, or whether the trough is connected at its ends to another, forming a complete electrolytic circuit in which a current is induced by some external means as in Mr. Marvin's apparatus, that is, without electrodes. In other words, to put it in unscientific language, the liquid in the middle certainly cannot know, nor does it care, whether the current is caused by electrodes or whether it is produced in some other way. Hence, the nature of the conduction in that part of the liquid is in my opinion exactly the same whether there are electrodes or no electrodes.

DR. CARHART: And therefore it is electrolytic.

MR. HERING: That is the case in my opinion.

DR. N. S. KEITH: Mr. President, it seems to me, that our nomenclature is deficient. If we are to accept in this matter that Faraday's term electrolysis, and its derivatives—electrolytic, etc., is confined entirely to analysis, why do we talk about electrolytic action taking place in the plating bath or in the refining? We speak of refining copper by electrolysis. What term have we for synthesis? What term have we to show that composition takes place, as well as decomposition? Some time ago I read a paper before the British Institution of Electrical Engineers and fortunately, or unfortunately, I entitled my paper "The Electrolysis of Gold." There was considerable discussion in the electrical journals. Some said I should say the "Electrolysis of the Solu-

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tion of Gold." Well, I took the ground that distinction between analysis and synthesis should be made, or my term was allowable from usage. I stood up as best I could for my position—call it a mistake or inadvertence—and there was never any decision made. I took the ground that if I was wrong the nomenclature was deficient. I still think so, and I would like to have an expression of opinion, if it is agreeable, from any of the gentlemen here.

MR. HERING: If we could only generate a direct current in such a closed circuit of an electrolyte, we could readily tell, because we might then interpose a diaphragm and by the different migration velocities of the two ions, we could tell whether the action of the current is the same when it is induced in the electrolyte itself as when it is led in by means of electrodes. There are probably other ways also, by which the presence of a direct current could be demonstrated.

MR. REED: In what way would the introduction of the diaphragm with a direct current prove anything?

MR. HERING: Most ions travel with their different velocities through the diaphragm; there would therefore be a concentration of one of the ions on one side, and a concentration of the other on the other side.

MR. REED: According to the theory of electrolytic dissociation that would not be possible, even with the diaphragm, because the number of positive and the number of negative ions in any part of the solution must always remain equal. You cannot effect any separation in that way. Even if that were true, there would be no way of detecting the truth.

MR. SMITH: Did I understand Mr. Reed to say, a little while ago, that he did not see any directive action in this experiment of Mr. Marvin's?

MR. REED: I certainly cannot see in Mr. Marvin's experiment any proof of a directive action or proof of the motion of ions.

MR. SMITH: I had an impression that you said you did not see a directive action on the liquid conductor which could produce the flow of current.

MR. REED: I think I said that there could not be any directive influence of the electrodes causing the ions to move in a particular direction in this case, because there were no electrodes.

MR. SMITH: But is there not a directive force acting on the

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ions? If there is electrolytic dissociation in the conductor you have negatively and positively charged ions, don't you, each with its electrostatic field; and when you superpose upon these an alternating magnetic field, don't you get a force exerted so as to produce a surging of the ions in one direction or the other, which would actually amount to an oscillation of charged ions through the circuit?

MR. REED: That is just what I wanted to have some proof of. What is the proof of this surging of ions or of any motion of ions? There is certainly nothing in the experiments of Mr. Marvin to show whether the ions are surging or not. These experiments do not even show that there are any ions. So far as these experiments show, there may be nothing but molecules present. Mr. Marvin has only proved that an electric current passes, that is, that the electrolyte is a conductor. This proves nothing in regard to the nature of the atoms or ions composing the conductor.

DR. CARHART: I rise with respect to nomenclature. I submit that if the electrolytic dissociation theory is correct, we might with great propriety say here that we have not metallic conductivity, but ionic conductivity.

MR. SMITH: I think that is just what we have. It seems to me that we have an ionic surging or an oscillation of minute electrostatic charges which, as Rowland showed, produces the effect of a current flow and which is bound to influence the secondary of the second transformer.

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A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 18, 1903, President Richards in the Chair.

NOTE ON A LABORATORY FURNACE.

By Barry MacNutt.

This furnace was constructed about two years ago with the idea of making an inexpensive experimental laboratory furnace of the Siemens type, in which crucibles of different sizes could be used.

The electrodes consist of a graphite crucible and a vertical carbon rod extending into the crucible and capable of being raised or lowered at will. Either the crucible or the rod may serve as anode or cathode. For this purpose a reversing switch is placed in series with the furnace circuit. Also, by means of a double throw switch, alternating or direct current may be used.

The crucible is supported upon a base which is made as follows: A number of arc lamp carbons were put together into the form of a cylindrical bundle, about 7 inches diameter, and surrounded by a retaining jacket of sheet iron. Wires from a stranded cable (of about 100,000 cir. mils cross-section) run up between the carbons and are pressed against the carbons by the squeezing of the retaining jacket. The interstices between the carbons are filled with crushed arc lamp carbons. The outer carbons of the cylindrical bundle extend about an inch above the others, forming a shallow cup on the top of the bundle. This cup is filled with finely crushed carbon. The crucible to be used is pressed down into this crushed carbon, making electrical contact through the rods to the stranded cable. This cable forms one terminal of the furnace. The cylinder with its retaining jacket is mounted in a block of cement, about one-half of the cylinder being embedded in the cement. It may be seen that a crucible of any diameter up to the inside diameter of the shallow cup may be used with this base.

The vertical electrode consists, in most cases, of a rectangular carbon, ¼ x 1 x 12 inches, and is connected to another stranded cable by means of clamps. Various sizes of crucibles, up to 5 inches outside diameter, have been used.

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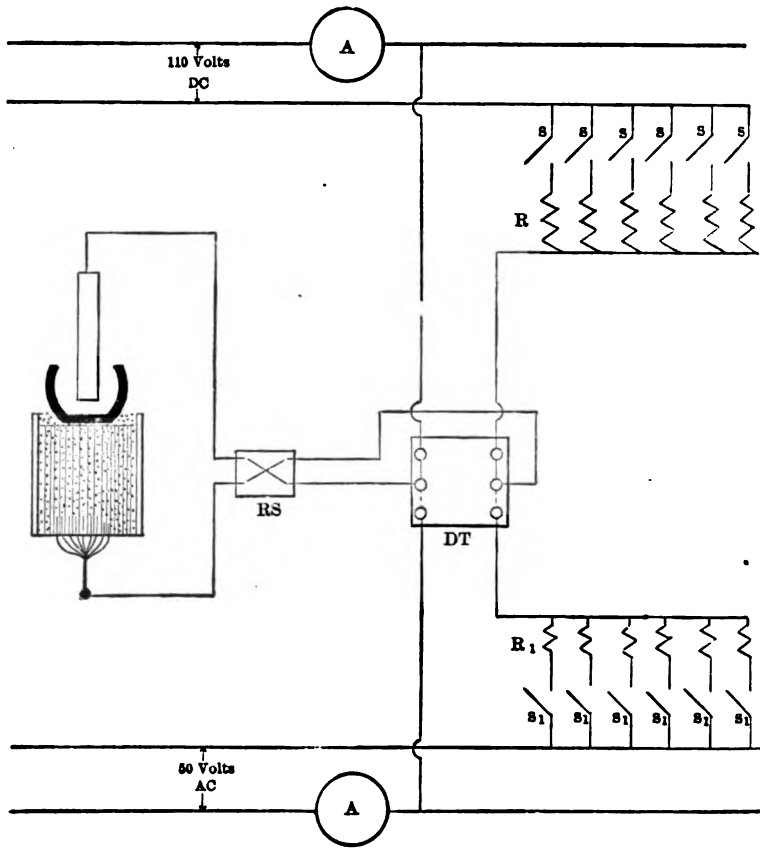
Different-sized vertical electrodes may be substituted to suit the crucible used.

150 amperes direct current at about 40 volts is the current usually employed. The current is regulated by cutting in parallel



resistances. Each resistance cut in increases the current by about 25 amperes.

With the alternating current connections, 200 amperes at 30 volts is the maximum current used, and the same method of varying the current is used as with direct current connections.

No difficulty was experienced in constructing the furnace and it was built at a low cost. It has worked satisfactorily, particularly with crucibles of about 1½ inches inside diameter. It has been found expedient to surround the sides of the crucible with fire-clay to prevent radiation.

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APPENDIX

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A Lecture delivered before the American Institute of Electrical Engineers and the American Electrochemical Society, in the Chapel of the College of the City of New York, April 17th, 1903.

RADIUM AND OTHER RADIOACTIVE SUBSTANCES WITH A CONSIDERATION OF PHOSPHORESCENT AND FLUORESCENT SUBSTANCES. THE PROPERTIES AND APPLICATIONS OF SELENIUM AND THE TREATMENT OF DISEASE BY THE ULTRA VIOLET LIGHT.

BY WILLIAM J. HAMMER.

The author of this paper has endeavored to exemplify certain fundamental principles connected with the phenomena upon which he has treated; and in considering these subjects, all of which may be said to be on the borderland of science, to bring out by means of experiments, lantern slides and illustrations which accompany the paper, the practical and commercial side. He entertains the hope that the matter herewith submitted will prove of interest to the members of the societies before whom he has the honor of appearing, and may serve in some slight degree to stimulate investigations in these most promising fields.

Fluorescence and Phosphorescence.

Sir George Stokes has given the name of " Fluorescence " to the phenomena which certain substances present in altering the very short waves of ultra-violet light, which are invisible, and transforming them into waves of longer length so that they become visible to our eyes.

In electrical parlance a fluorescent substance might be termed a step-down transformer or perhaps more correctly a frequency changer for light waves. Stokes, as a result of his investigations, framed this law, " When the refrangibility of light is changed by fluorescence it is always lowered and never raised "—in other words, the waves emitted during fluorescence are always longer than those which are absorbed, thus causing fluorescence. There are, in fact, cases where the frequency of

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the radiations is increased; but where there is such an exception to Stokes' law some sort of chemical reaction occurs.

The lowering of the frequency of certain ultra-violet radiations, so as to render them visible, was known to Brewster in 1833 and Herschel in 1848, the former terming it internal and the latter surface dispersion; but it was first explained and the name given to it by Stokes in 1852, after a form of fluorspar.

In the case of fluorescence, the emission of the light lasts only so long as the substance is stimulated by the incident beam; but in the case of the phosphorescence, the emission of light continues or persists after the stimulation has ceased, or the original source has been removed. The word phosphorescence is from the Greek " phōsphoros," meaning light bearer.

Prof. E. Wiedemann has suggested the name " luminescence," to cover fluorescence, phosphorescence and phenomena of that character possessed by many substances whose light emissions are unaccompanied by flame or by the temperature of ordinary light waves; but this term can hardly be made to cover the Becqueral rays emitting from radioactive substances.

I have here to-night a collection of tubes containing fluorescent liquids, such as petroleum, quinine, Magdala red, eosine, uranine, saffronine, paviine, æsculine, amidophthalic acid, fluorescine, rhodamin, etc., all of which show most beautiful changes in color when viewed by direct and transmitted light.

I also have some of the fluorescent hydrocarbon " thalleen," prepared by the late Prof. Henry Morton, and some of those most beautiful fluorescent substances, resorcorufin and resorcin blue, for which I am indebted to Dr. Geyer of Steven's Institute. Fluorescent substances are particularly beautiful in the ultra-violet light; for instance: The yellow fluorescene becomes a most beautiful green; the orange colored eosine becomes gamboge; the crimson color of Magdala red a bright scarlet; the straw colored æsculine becomes a pale blue; the transparent and colorless quinine gives its characteristic blue surface tint; the paraffin oil a beautiful blue; and the various other substances giving a beautiful surface color quite different from that of the interior of the solution.

Small pieces of horse-chestnut bark or bark of the ash tree placed in a dilute ammoniacal solution produce a most beautiful fluorescent effect, as the dyeing material descends slowly through the liquid.

Flowers painted with these fluorescent substances on card-

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board produce a most beautiful effect when light screened by dark blue or violet glass is thrown upon them.

Sodium vapor fluoresces brilliantly in sunlight.

I also have here samples of tungstate of calcium, platino-barium cyanide, sulphide of zinc, and similar preparations which have been extensively used in the fluorescent screens for X-ray work.

Here is a specimen of Willemite which when exposed to the ultra-violet light produced by the bright snappy condenser spark between these iron electrodes shows a magnificent fluorescence.

Here is a card with words written with a solution of platino-barium cyanide which fluoresces beautifully when exposed to the ultra-violet light of the iron arc, especially when shielded by the accompanying colored glass plates.

I have also one of Prof. R. W. Wood's interesting ultra-violet screens, consting of four isplates of cobalt glass between which are gelatine films containing nitroso-dimethyl-analine with copper oxide, which screen when employed in front of the arc lamp renders beautifully fluorescent a lump of uranium nitrate held in the focus of the invisible rays.

Through the courtesy of Dr. Von Recklinghausen, I am enabled to show you a Cooper-Hewitt tube which is enclosed in a screen soaked in rhodamin, the best substance which thus far has been found which is fluorescent in the light of the mercury arc.

It is well known that many bodies become red hot at a temperature of between four and five hundred degrees Centigrade, and to make them white hot a temperature of between eight hundred and a thousand degrees is necessary; but there are many substances which are phosphorescent and which possess the property of giving off considerable light without sensible heat.

I have here some samples of two phosphorescent substances which have been known for many years—one of them a sulphide of barium or Bolonese phosphorus, and the other a sulphide of calcium or Canton's phosphorus. The former was discovered in 1602 by Casciarlo, a shoemaker in the city of Bologna who prepared it by the partial calcination of a certain powdered heavy spar mixed with a little flour meal, which he roasted in the furnace; and found afterwards that when exposed to sunlight it would shine in the dark. This preparation was succeeded by the discovery of John Canton, who calcined oyster shells with charcoal and meal in a closed crucible, thus producing a brilliant phosphorescent substance called after his name.

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Phosphorescence by insolation—or exposure to sunlight—has been extensively investigated by Prof. A. E. Becquerel and Dr. John W. Draper.

Practically all substances in nature are phosphorescent, and although some of them remain phosphorescent for only one ten-thousandth of a second, others retain their phosphorescence for hours.

One may expose sulphide of calcium to sunlight, and after placing it in a dark room for six weeks it will still affect a photograph plate.

Phosphorescence may be stimulated in many ways—by combustion, pounding, rending, friction, by the vibrations from sources of heat, light or electricity; and these various phosphorescent substances are very susceptible to temperature changes.

Various substances also phosphoresce while undergoing crystallization.

I have here a large sheet of cardboard which has been prepared for me by Messrs. Devoe & Company, which is covered with seven coats of Balmain's Luminous Paint or poly-sulphide of calcium, with perhaps a trace of bismuth and mixed with aerated varnish; and it has been put through hot calender rollers. You will note that this phosphoresces most beautifully when excited by burning this piece of magnesium wire before it, or by focusing the arc light upon it. This phosphorescence soon dies out, however; but upon placing my hand against the sheet, the heat of my hand has caused the card to brilliantly phosphoresce. A cold object placed against the cardboard will very much lessen the phosphorescence at that point.

When I place this bust of Franklin between the arc light and the phosphorescent cardboard, you will note I can thus produce a fine silhouette of that distinguished philosopher.

I have prepared for your consideration a number of objects coated with phosphorescent substances. When I burn this piece of magnesium wire in front of this card, or hold it before the arc light, you will note the initials of the A. I. E. E. and the A. E. S., the two societies before which I have the honor of appearing to-night, shine out brightly. I also have a number of incandescent lamp bulbs, coated internally and externally with phosphorescent substances, which you will note give considerable light when stimulated by the burning magnesium; or by turning on the electricity supplying certain of the lamps.

I remember nearly twenty years ago having cut out tiny stars

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from cardboard and painted them with luminous paint, and arranged them on the ceiling of my bed room to represent certain of the principal constellations in the heavens. These stars would absorb the light during the day time, and at night would represent an appearance as though the roof had been removed and one was looking at the stars in the sky.

I have here a philosophical toy which I made years ago, with which I can show the varying phases of the moon. I have taken a 25 cent globe, and painted half of it with black Japan, as representing the dark side of the moon which is never seen, the other half I have painted with a number of coats of luminous paint; and by exciting the phosphorescence of this half by the burning magnesium, you will see that by slowly turning the globe around, a perfect representation of the varying phases of the moon occurs.

I hold in my hand here a long tube coated inside with sulphide of calcium, which makes a beautiful wand, which an orchestra leader might use in a dark scene. I remember years ago fixing up a vacuum tube and coil for use as a baton in the dark scene in Gilbert & Sullivan's Opera of Ruddigore, and fearing lest the complaisant leader be some day knocked off his stool by the 8-inch coil.

Here are a couple of postal cards which I secured in Europe showing the Blue Grotto at Capri. They are printed with phosphorescent paints; and on exposing them to the light, you will see they are exceedingly pretty.

Prof. Dewar has shown that egg shells, feathers, ivory and paper become brilliantly phosphorescent if they are cooled to about 200 degrees below zero by use of liquid air, and then exposed to light. Many bodies seem to possess this power of absorbing energy at low temperatures and giving off light at higher temperatures In fact, Dewar has observed that at a temperature approximately that of the boiling point of oxygen (184° C) all bodies, even living tissues, become phosphorescent.

I have here a collection of forty or more glass tubes containing various phosphorescent substances which, when I burn this magnesium before them, you will note become brilliantly phosphorescent, showing red, yellow, green, blue, and in fact, all the colors of the spectrum. The sulphides of calcium, barium, strontium, zinc, etc., largely enter into their composition. I also have here some fine particles of fluorspar, which, when scattered on this hot plate, glisten like fire flies.

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A similar effect may be produced by quinia or its sulphate which when spread on a sheet of paper and laid on a hot metal plate in a dark room, shows a remarkable phosphorescence which develops at the edges and spreads to the centre.

Boracic acid fused and allowed to cool breaks into small pieces, and along the cracks phosphorescent light appears. Potassium sulphide fused with cream of tartar shows the same phenomenon.

Phosphorescent ether may be prepared by digesting phosphorus in ether for some days in a tightly corked bottle, and when a lump of sugar is dipped into this and dropped into a glass of water, the surface appears quite luminous.

The stream of particles, so thoroughly investigated by Prof. Crookes, was given the name of " Cathode rays " by the Germans, as a protest against Crookes' theory of molecular streams propounded by him at the British Association meeting of 1879; Lord Kelvin has told us that the smallest particle which can be observed by the most powerful microscope contains 18 to 20 million atoms, and although until recently the smallest particle we could conceive of was the atom of hydrogen, this being the lightest of gases, Prof. J. J. Thomson has now shown us that these atoms may constitute a thousand fragments, or as he calls them, " corpuscles," and Crookes showed us, and Villard of Paris recently demonstrated conclusively that the Cathode rays consist of a stream of these hydrogen corpuscles negatively charged and moving at a speed approximating 70,000 miles per second; and as illustrating the complexity of an atom, I am reminded by Prof. Hallock that the late Prof. Henry Rowland once said that a Steinway grand piano was a comparatively simple piece of mechanism compared with an iron atom.

Prof. Crookes has shown many notable experiments in which substances have been caused to phosphoresce inside of the Crookes' tube by the molecular bombardment of " Cathode rays "; and I have here some fine Crookes' tubes containing red and white coral, rubies, calcite, lava, etc., which you will note phosphoresce finely. (I am indebted to Messrs. Queen & Co. for certain of these.

Prof. Crookes has made a diamond so phosphorescent inside of a Crookes' tube, as to give a full candle power of light. Rubies emeralds, corals, fluorspar, lime and many other substances similarly phosphoresce in the Crookes' tube.

I have here a Crookes' tube containing calcined sea shells,

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which, on connecting to the induction coil, is caused to give off a most brilliant light, and the globe and contents to phosphoresce long after the current is shut off.

Here again I have a tube containing four separately exhausted sections, which are filled with phosphorescent substances, and a tiny tube passing through all of the partitions of the tubes, and being connected with the electrodes at the end. On connecting this to the induction coil a luminous gaseous stream is seen in the tiny tube, and the discharge accompanying it affects powerfully the phosphorescent substances which, you will note, are colored green, yellow, and blue, after the current is shut off.

I have here also a Crookes' " radiometer," the vanes of which are painted with phosphorescent substances, and on connecting the radiometer to the coil the electricity rotates the vanes and causes them to become highly phosphorescent.

At a meeting of the INSTITUTE on January 3, 1902, through the courtesy of Mr. Edison, I was enabled to present some of Mr. Edison's tungstate of calcium lamps which have sometimes been called Edison X-ray lamps. These lamps were Crookes' tubes, the interior walls of which were coated with fused crystals of tungstate of calcium, which were caused to phosphoresce most dazzlingly when they were connected to an induction coil. Through an accident to my large coil, I was unable to show these tubes working as perfectly as I should have liked; and to-night I will show you as an evidence of good faith some of them operating as they should operate, and giving a most powerful light. Incidentally, I am going to show you that this cannot properly be called an X-ray lamp although a form of X-ray tube is employed, as it is not the X-rays outside but the cathode rays inside of the tube which produce the phosphorescence. This tube which I have here and which I have coated with tungstate of calcium and platino-barium-cyanide on the outside, I will now place underneath an ordinary Crookes' tube, that it may be exposed to the X or Roentgen rays; and you will see that while the coated surface fluoresces, as any fluorescent screen will when exposed to Roentgen rays, the moment these rays cease there is absolutely no phosphorescent effect, there being no persistence of the luminescence.

Now, another thing which I think I can show you is that, while cathode rays produce by their action on the interior wall of the glass tube a secondary effect of ether pulsations on the

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exterior which are Roentgen or X-rays, I can now produce the converse of this by bombarding the outside of the Edison tube by the Roentgen rays from the Crookes' tube, and you will see then that I have caused cathode rays to be stimulated in the interior of the tube which is merely held near it, causing the tungstate of calcium to become brightly phosphorescent; and you will note that I can deflect the cathode rays with a magnet. I believe this is the first time this conversion of Roentgen rays into cathode rays has been accomplished and is rendered possible by this form of tube.

There are many commercial applications which may be made of this curious property of phosphorescence. Life buoys have been painted that they may be seen when thrown overboard; sheets of cardboard, such as I have shown you, have been used to give light in powder magazines. I have also suggested painting projectiles with luminous paint for use at night; phosphorescent clock and watch dials have been made in large numbers, and it has been suggested to make house numbers, door knobs and escutcheons for key holes of such materials, cover the walls with luminous paper, and even paint the houses with luminous paint.

The taps or keys of incandescent lamp sockets and switches might be made of glass containing phosphorescent material, or the cases painted as I have here done, so that they could readily be seen in the dark; and doubtless certain phosphorescent substances might be used to considerable advantage in connection with various types of vacuum tube lighting and for vacuum tubes used in connection with wireless telegraphy.

I hold in my hand a tiny tube which I secured in Paris, which contains what is perhaps the most brilliant phosphorescent substance that has yet been discovered. It is a special preparation of sulphide of zinc. Here is a second tube containing some of the sulphide of zinc, which also has mixed with it some radium.

A tube of this mixture may be put away in the dark for years, and the radium will act on the zinc, causing it to phosphoresce brilliantly.

Who will say that we shall not some day find a substance which will be so powerfully acted upon by the emanations from radium that it may be used as a source of light?

Here I have a tube which I have made on the suggestion of Prof. Curie, consisting of two bulbs with a stop cock between, in one of which may be placed sulphide of zinc, or similar substances, and in the other radium; and in this manner the radioactivity of various substances may thus be investigated.

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A tube containing chloride or bromide of silicon and exhausted to 12 or 15 mm., and sealed, will when rubbed briskly with silk glow in one case a rose color and in the other a greenish yellow.

I hold in my hand here two Geisler tubes, each containing an inner tube with beaded surfaces. In each of the outer tubes is a small amount of quicksilver; and in one tube nitrogen gas, and in the other carbonic acid gas. By shaking these tubes rapidly the friction of the quicksilver against the glass produces electricity, which causes the gas to become luminescent. Various other gases may be thus employed, producing different color effects.

It has been suggested that life buoys could be equipped with a number of mercury tubes, circular or otherwise, and set in different positions, so that the rolling of the buoy in the sea would constantly agitate the mercury and render the tubes luminous.

Here is a tube containing mercurial salts, which changes greatly the color of its phosphorescence by heating the tube in alcohol flame.

In this box I have a large spiral glass tube which is expanded into bulbs at various points throughout its length. This tube, for which I am indebted to my friend Dr. Geyer, contains sulphuric anhydride; and you will note when I connect this to the induction coil and send a discharge of electricity through it that the gas inside of the tube becomes phosphorescent and remains so for a considerable period after the electricity is cut off.

I have here a bottle containing phosphorus and olive oil, which you will see becomes most brilliantly phosphorescent when I withdraw the stopper, and allow the air to enter the bottle. The phosphorescence in this case is due to combustion, or to the oxidation of the liquid. I can also write phosphorescent characters on this ground glass plate wet in hot water with this stick of phorphorus. Other forms of phosphorescence are caused by chemical changes or the slow combustion of decaying vegetable matter or decaying fish.

Occasionally clouds show a phosphorescent light at night; snow is phosphorescent after exposure to sunlight, and no doubt many substances retain during the night the phosphorescent light imparted by the sun's rays during the day.

There are also many insects, such as fire flies and glow worms, and many deep sea fishes which have the properties of producing phosphorescence. Phosphorescence is exhibited among other animals by the infusorian noctiluca, marine radiates, polyps, etc., which are the principal causes of phosphorescence of the sea.

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In Fig. 1, is shown an illustration of the " Pyrophorus Noctilucus." This tropical beetle has been most carefully studied by Prof. S. P. Langley and F. W. Very, and the efficiency of the light given off tested by the Langley bolometer; and they have demonstrated that practically all the energy which its phosphorescence represents, appears as light; and the light given off by this insect is the most efficient light known, it being produced at about one four-hundredth part of the cost of the energy which is expended in the candle flame*.

Sir Oliver Lodge says if the secret of the firefly were known, a boy turning a crank could furnish sufficient energy to light an entire electric circuit.

And Prof. Langley says, " There seems to be no reason why we are forbidden to hope that we may yet discover a method (since such a one certainly exists and is in use on the small scale)

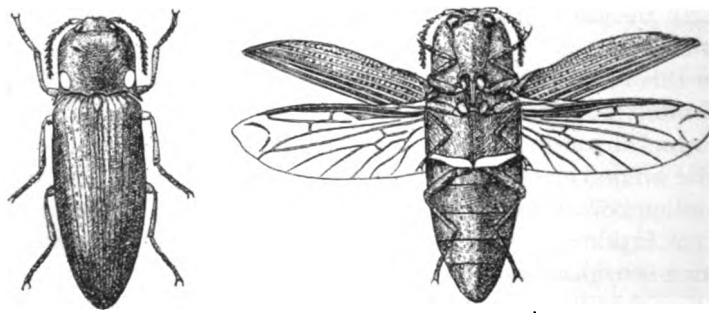

FIG. 1.—"Pyrophorus Noctilucus " (life size), the Producer of the Cheapest Form of Light Known.

of obtaining an enormously greater result than we now do from our present means of producing light."

Langley believes the light of these insects is due to chemical action, as it is decreased by nitrogen which checks combustion, and is increased by oxygen which increases combustion, and furthermore, the product is apparently carbon dioxide.

We also may produce phosphorescence by rubbing crystals together, or by friction of other bodies, or by cleavage, such as fracture of lump sugar in the dark.

Among plants, phosphorescence was first recorded by A. Linnæus, whose daughter discovered it in the nasturtium. Phosphor-

* " On the Cheapest Form of Light," by S. P. Langley and F. W. Very, No. 1258 Smithsonian Misc. Coll.

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escence or flashes of light are often observed, especially just after sunset, in the common red and yellow marigold, the tuberose, sunflower, poke weed, martagon-lily and the poppy. The root stock of khus-khus grass and the sap of certain tropical vines and subterranean plants, some liverworts, ferns, mosses, fungi and algæ, and the mycellum of fungi in decaying wood phosphoresce. This phosphorescence is said to be due to slow decay and oxidation, either in the mycelia or fructifications of the fungi. Heat and dryness soon dissipate it.

Having considered certain of the phenomena of phosphorescence and fluorescence, I wish now to call your attention to these remarkable substances which have recently been discovered, which give off light the moment they are created, without having to be stimulated by any form of heat, light, electrical or other vibrations, so far as we are at present cognizant of, and these substances are attracting a great deal of attention, and are likely to teach us more about the constitution of matter, and the co-relation of the vital and physical forces, than any substances which have been created since the world began. I refer to "Radium, Polonium, Actinium and Thorium."

Radium and Other Radioactive Substances.

Prof. Henri Becquerel.
From a portrait presented to the author.

To the discovery of M. Henri Becquerel, member of the Institute, of France in 1896, of those remarkable radiations emanating from uranium, the science, if we may so term it, of radioactivity, owes its foundation

Great importance must, however, be attached to the previous investigations into the phenomena produced on the interior and exterior of vacuum tubes of various kinds by such men as Varley, Hittorf, Crookes, Lenard, Roentgen, Hertz, J. J. Thomson, Goldstein, Schmidt, Ebert, Wiechert, Geissler, Kaufmann, Puluj, Perrin, Villard, Wien, Wiedemann, Majorana, Birkland, Deslandres, Poincaré, Edison, Tesla, Rowland, Michelson

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E. Thomson, Moore, Rollins, Campbell-Swinton, and others, which investigations had already wrested from Nature so many secrets bearing upon the constitution of matter and paved the way for the Becquerel rays

Two important links in the chain were supplied by the experiments of M. Henry[1] and M. Niewenglowski[2]. The former showed that phosphorescent sulphide of zinc penetrated black paper and affected a photograph plate, similar to Roentgen rays; and the latter in his experiment replaced the usual cover of a loaded photographic plate holder by a thin sheet of aluminum; on top of this he placed four glass squares sprinkled over with sulphide of calcium rendered phosphorescent by exposure to sunlight. A jeweller's glass bell jar was put over each plate, and the whole apparatus was then placed in a dark room for twenty-three hours. On developing the negative, the plate showed an excellent image of the squares of glass and the bell glass covers which had been made through the aluminum, a substance heretofore supposed to be entirely opaque to light, the white line shown bordering the squares of glass (where the plate had not been affected) indicated that the rays had here been bent or refracted in passing through the edge of the glass, demonstrating that he was only dealing with ordinary light rays.

Subsequently, Prof. Becquerel investigated the effect of phosphorescent substances on photographic plates covered with black paper, such as is used for covering X-ray plates; and which while transparent to X-rays is impervious to ordinary light waves (a plate so protected may be left in the sunlight for twenty-four hours); and he exposed various uranium salts to sunlight to try their effect, at times placing an aluminum, copper or glass plate between the paper and the photograph plate or film. On one occasion after he had placed some double sulphate of uranium and potassium on a photographic plate, the weather became stormy, and he placed his plate with the uranium salts upon it in a drawer, where it remained for several days on account of continuance of the cloudy weather. It then occurred to him to develop the plate; and much to his surprise he found a well-defined impression upon the plate, and this caused without any effect of phosphorescence due to exposure to sunlight. This

1. *Comptes Rendus*, Feb 10, 1896. Vol. cxxii., p. 312.
2. *Ibid*, cxxii., p. 386.

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led to his discovery and investigation of the remarkable radiations which have since been known by his name*.

I have here some samples of the first substances employed by Becquerel, consisting of double sulphate of uranium and potassium and double sulphate of uranium and ammonium, for which I am indebted to the courtesy of Dr. C. F. Chandler, of Columbia University

Peligot in 1840 succeeded in isolating metallic uranium from the chloride. Well known forms of it are also uranium arsenate, uranium carbonate, uranium niobate, uranium phosphate, uranium silicate and uranium sulphate. Uranium was first discovered in 1789 by the German chemist Klaproth, he naming it after the planet " Uranus." I have here various forms of this uranium and also some metallic uranium prepared in the electric furnace by Moissan, which is more powerful than any other form of uranium.

Uranium, although widely distributed, is never found in large amounts, and forms several minerals. The commonest of these is " uraninite," commonly known as " pitchblende," which is a compound oxide containing 81½ per cent. of uranium, 4 per cent. of lead and ½ per cent. of iron with oxygen and water, and sometimes magnesia, manganese or silica.

The pitchblende which contains the largest percentage of radioactive material, which has thus far been discovered, is the Bohemian pitchblende. It is also found in Saxony in small pockets, and a distinct vein of it has been found in Cornwall, England. Prof. Curie informed the writer that he had secured some excellent radioactive pitchblende from the United States (Colorado).

The ore as mined in Cornwall yields 18 per cent. to 20 per cent. of the metal, this being the most important source, and this is usually put on the market in the form of uranium sesqui-oxide, and is largely used for giving porcelains a velvety black when heated in the annealing fire, and to some extent for imparting a greenish yellow fluorescence to glass. It has also been suggested to utilize it on account of its high resistance in connection with incandescent lighting.

Following the original discovery of the Becquerel radiations in 1896, came the discovery in 1898 of " Polonium," by Prof. Pierre Curie and Mme. Sklodowska Curie, who in investigating Becquerel

* *Comptes Rendus*, Feb. 24, 1896. Vol. cxxii., p. 420.

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radiations from uranium found some samples of pitchblende, from which the uranium is extracted, which was much more powerful than any uranium they had found, being four times the radioactivity of metallic uranium. Concluding naturally that the Becquerel radiations were due to some unknown substance in the pitchblende they commenced a most painstaking search for it, and discovered a substance associated with bismuth, which it resembled very much in its chemical characteristics, to which Mme. Curie gave the name " Polonium," after her native land, Poland.

I have here perhaps the only sample in this country at present of metallic polonium, which in color resembles somewhat the particles of nickel; and here also is some sub-nitrate of polonium.

Where substances are referred to as possessing a certain "radioactivity," for instance 300, it means that the radiations are 300 times as powerful as the original radiations emanating from uranium, which were discovered by Becquerel, and which are taken as a standard of comparison.

The two tubes which I have here to-night are of the sub-nitrate and metallic form, and possess a radio-activity of only about 300. The sub-nitrate form is a white powder, and the metallic, as said. resembles in appearance particles of nickel.

Polonium is precipitated by hydrogen sulphide.

Polonium apparently loses its power much more rapidly than radium; and the Curies have not been able to prepare any in which the rays have been deviable, although Giesel has prepared a form possessing both deviable and non-deviable rays. And Elster states that when polonium is placed in a vacuum, the rays may be deviated by a magnet to a greater extent than those of radium.

Polonium passes more rays through aluminum than do the rays from uranium; but Crookes has shown that they do not penetrate glass, as in the case of radium, and they are readily absorbed by minerals, and readily cut off by thin paper. They are readily absorbed by quartz, fluoride and mica, whereas these substances are freely penetrated by both radium and uranium.

In the same year in which polonium was discovered, those remarkable investigators, M. and Mme. Curie and M. Bemont, succeeded in isolating a second substance found in pitchblende, which was associated with barium and possessed many of the chemical and other characteristics of that substance, and to this they gave the name " Radium." Of this we shall treat later.

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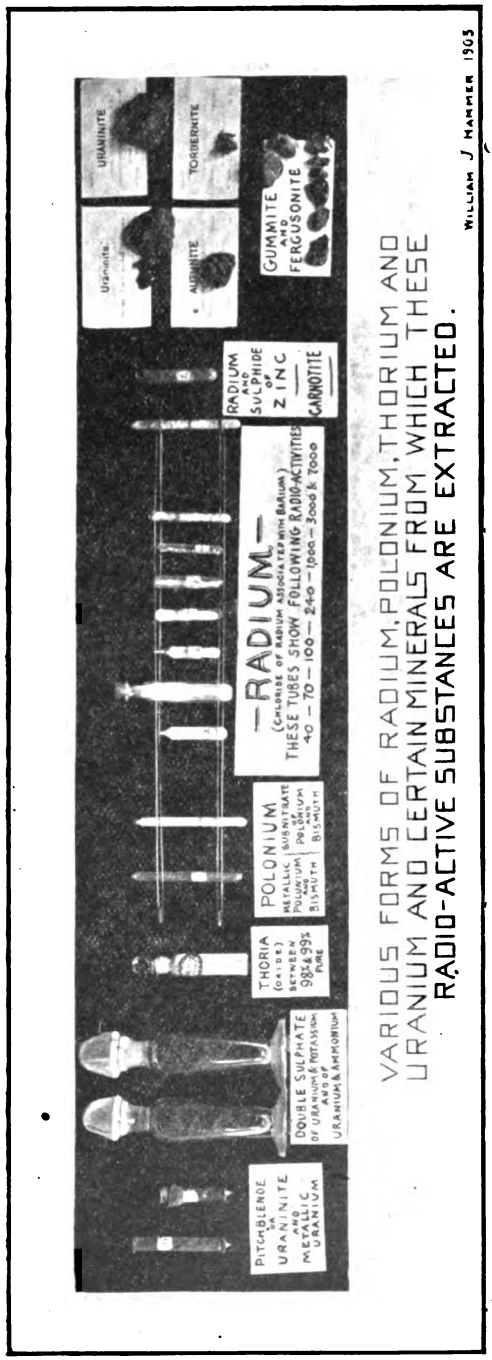
VARIOUS FORMS OF RADIUM, POLONIUM, THORIUM AND URANIUM AND CERTAIN MINERALS FROM WHICH THESE RADIO-ACTIVE SUBSTANCES ARE EXTRACTED.
WILLIAM J HAMMER 1903
PITCHBLENDE OR URANINITE AND METALLIC URANIUM
DOUBLE SULPHATE OF URANIUM POTASSIUM AND URANIUM & AMMONIUM
THORIA (OXIDE) BETWEEN 98½ & 99% PURE
POLONIUM METALLIC BISMUTHATE POLONIUM AND BISMUTH
—RADIUM— (CHLORIDE OF RADIUM ASSOCIATED WITH BARIUM) THESE TUBES SHOW FOLLOWING RADIO-ACTIVITIES 40 — 70 — 100 — 240 — 1000 — 3000 & 7000
RADIUM SULPHIDE OF ZINC
CARNOTITE
GUMMITE AND FERGUSONITE
AUTUNITE
TORBERNITE
URANINITE
Uraninite

FIG. 2.—Radioactive Substances.

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In 1899 was discovered the third substance in pitchblende, which possessed the chemical and other characteristics of thorium with which it was associated, and to this Debierne gave the name "Actinium." It is precipitated by ammonium sulph-hydrate. Crookes states that actinium is identical with the substance which he had isolated from uranium and to which he gave the name "uranium X." The rays from actinium are deviable.

Of the three substances to which I have referred, radium is by far the most important and is of extraordinary interest. It is doubtful whether any substance has been discovered in the history of the world of such stupendous interest and importance and possessing such puzzling characteristics as radium, which seems so at variance with well-established scientific theories as to the constitution of matter.

In Fig. 2 are shown in consecutive order from left to right, a tube containing pitchblende, or uraninite, from which radium, polonium and actinum as well as uranium are extracted; a tube containing metallic uranium made in the electric furnace by Moissan; two flasks containing double sulphate of uranium and potassium, and double sulphate of uranium and ammonium, these being the original salts of uranium with which Becquerel experimented when he discovered the Becquerel rays ; a tube containing thorium, the most radioactive substance next to radium; two tubes of polonium and bismuth, one tube of metallic polonium and the other sub-nitrate of polonium ; seven tubes of chloride of radium associated with barium ranging in radioactivity from 40 to 7,000; a tube containing radium and phosphorscent sulphide of zinc ; and a tube containing carnotite, which, together with the samples shown of uraninite, autunite, torbernite, gummite and fergusonite, are among the mineral substances which are rich in radioactive materials. Other active minerals are orangite, euxenite, broggerite, cleveite, monazite, samarskite, xenotime, æschynite, niobite, arrhenite, hielmite, sipilite, chalcolite, etc.

In Fig. 3 the two tubes of polonium and the seven tubes of radium are shown about two-thirds their natural size.

Radium actinium and polonium, Prof. Curie states, possess an activity which is a million times that of uranium. Prof. Curie says radium emits exactly the same quantity of Becquerel rays when in the liquid air as it does at normal temperature of the atmosphere. The luminosity of the chloride of radium is stronger in the liquid air than in the atmosphere at a normal temperature.

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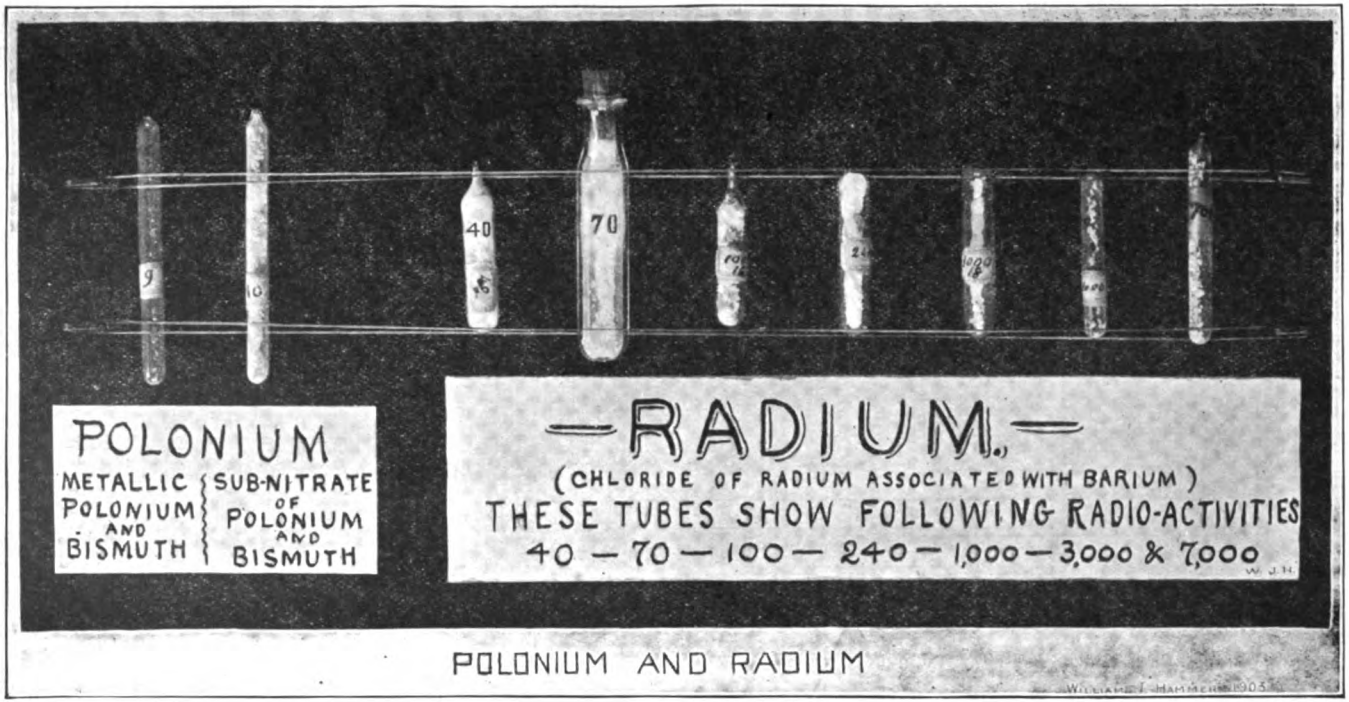
POLONIUM
METALLIC POLONIUM AND BISMUTH
SUB-NITRATE OF POLONIUM AND BISMUTH
—RADIUM.—
(CHLORIDE OF RADIUM ASSOCIATED WITH BARIUM)
THESE TUBES SHOW FOLLOWING RADIO-ACTIVITIES
40 — 70 — 100 — 240 — 1,000 — 3,000 & 7,000
40
70
POLONIUM AND RADIUM

FIG. 3.—Showing two tubes of Metallic Polonium and Bismuth and Subnitrate of Polonium and Bismuth, and seven tubes of Chloride of Radium and Barium in the possession of the author. (About two-thirds natural size.)

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My friend, Mr. R. R. Bowker, whom I met in Paris last Fall, told the writer that he had shortly before that been dining seated between Lord Kelvin and Prof. Becquerel, and that Lord Kelvin had turned to him and said, that the discovery of Becquerel radiations had placed the first question mark against the principle of conservation of energy which had been placed against it since that principle was enunciated.

Within the past month great interest has been attracted by the statement made by Profs. Curie and Laborde that radium maintains its own temperature at 1.5 Centigrade above its surroundings, this being equivalent to stating that half a pound of radium salt would evolve in one hour sufficient heat to equal that caused by the burning of one-third of a cubic foot of hydrogen gas; and that the heat evolved from pure radium salt is sufficient to melt more than its own weight of ice every hour. This evolution of heat, it is claimed, is going on constantly for indefinite periods and leaving the radium at the end of months of activity as potent as it was at the beginning. The problem therefore confronts the world of solving how radium can constantly throw off heat without combustion or without chemical change, as Prof. Curie says it does.

Messrs. Curie and Laborde employed a thermo-electric couple of iron and constantin, one of whose junctions is surrounded by radioactive barium chloride and the other by pure barium chloride. They used two small bulbs of the same dimensions, one containing one gramme of radiferous barium chloride containing about one-sixth of its weight in radium chloride and the other bulb containing one gramme of pure barium chloride.

The junctions of the thermo-electric couple are respectively placed in the center of each bulb, surrounded by the substances. The bulbs are isolated in air within the center of two small identical enclosures, surrounded in turn by a third, which is thermally insulated, and maintains itself at a practically uniform temperature, and under these conditions variations in the surrounding temperature are felt in the same manner at both junctions and do not affect the indications of the couple. Messrs. Curie and Laborde both thus observed a difference of temperature of 1.5 degrees C. between the radiferous barium chloride and the pure barium chloride, the former having the higher temperature. (*Comptes rendus*, March 16, 1903).

In a letter recently received by the author from Prof, Curie bearing upon the question of heat given off by radium Prof. Curie writes as follows: " Since the time I had the honor to see

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you at our School of Physics and Chemistry I have continued to investigate into the radioactivity induced by radium and the way that radioactivity is disappearing in the course of time.

"In a study of another kind (in collaboration with M. Laborde) I found that the radium is setting off heat continually and in a very large amount; each gramme of the radium is setting off in each hour 100 small calories, or in other words it is setting off heat enough to melt in each hour its own weight in ice.

"Where is the source of this energy? Both Mme. Curie and myself are not able to go beyond some hypothesis; one of these consists in supposing the atoms of radium evolving and transforming into another simple body and despite the extreme slowness of that transformation which cannot be located during a year; the amount of energy involved in that transformation is tremendous."

The second hypothesis consists in the supposition that radium is capable of capturing and utilizing some radiations of unknown nature which cross the space without our knowledge."

Profs. J. J. Thomson and Rutherford advance the theory that there is a succession of chemical changes going on causing the spontaneous projection of larger masses of material at enormous velocities, and that while certain portions are constantly dying out and becoming inert other portions are constantly increasing in strength and power.

Someone has remarked that for years we have been extracting uranium oxides, and pouring down the waste pipes and into the dust bins the more interesting and precious radioactive substances.

Although radium, polonium and actinium have been termed new elements, in the case of polonium and actinium, they have as yet not been found in sufficiently pure state and in sufficient quantity to give a spectrum, and to prove conclusively that they are new elements. Prof. Curie has, however, stated emphatically that there is now no doubt of radium being a new element.

The tiny brown bulb which I hold in my hand is the duplicate of the one which Prof. Curie showed me at his laboratory last Fall, which contained the only sample of chemically pure radium in the world, this being between two and three one-hundredths of a gramme; and it was the spectrum of that sample, showing only the lines characteristic of radium, as tested by Demarcay, which demonstrated it to be a new element. And with this sample, also, the atomic weight for radium of 225 was determined. The

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atomic weight of the barium heretofore always associated with radium, but which in this sample had been eliminated, is but 157.

In answer to my inquiry as to its value, Prof. Curie said that 100,000 francs ($20,000) could not purchase this tiny sample.

I was enabled through the courtesy of Prof. Curie to secure from the Societé Centrale des Produits Chimique of Paris, some nine different preparations of radium and two of polonium, which I have here for your consideration. I was unable to secure any actinium; in fact, but a trace of this substance has thus far been secured.

If the lights are extinguished, and you will sit for a few moments in the dark, I will pass these tubes about the room that you may observe the bright light given off by certain of them. These samples which I have range from forty times the radio-activity of uranium (which is taken as a standard), up to 7,000.

The laboratory, where these substances are prepared, is under the control of Prof. Curie; and up to recent date, all radium of higher radio-activity than 7,000 has been retained for the experiments of M. and Mme. Curie and their associates; but I received a letter recently from Director P. Boulay of the Societé Centrale, in which I was informed that they will shortly put upon the market a preparation of radium, chemically pure or nearly so, at a cost of 30,000 francs ($6,000) per gramme or about $2,721,555.90 per pound.

Radium, while it has been spoken of as a metal, has never been secured in a metallic form, the usual form being as a chloride or bromide.

Prof. Curie told the writer that the result of all the work done in Germany and France in the past three years had only resulted in the securing of about one pound of radium; this including all grades or qualities. Prof. J. J. Thomson says there is far more gold in sea water than there is radium, polonium and actinium in pitchblende.

Prof. Curie took this ring which I have on my hand, which contains a small diamond, into his dark room and holding near it a small pill box containing about a gramme of radium, caused the stone to phosphoresce most beautifully. It was as if a lightened candle had been brought near to it. Prof. Curie remarked that this showed that the stone was a genuine diamond; and if it had been paste there would have been no effect produced, and that radium therefore constituted an excellent means for testing the genuineness of diamonds.

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According to M. and Mme. Curie, radium rays act in many ways like light. They reduce silver salts, peroxide of iron and bichromate of potash in presence of organic substances; they also color glass, porcelain and white paper, and they transform greenish yellow platino-cyanide of barium into a brown variety.

Giesel had prepared platino-cyanide of barium with a trace of radium. This spontaneously became brown, and it then polarized light like tourmaline. He also found that this colored rock salt just as cathode rays do, or the vapors of alkaline metals, and furthermore showed that radium salts, brought near the temples or to the closed eyes, produced a sensation of light.

M. Becquerel, referring to the chemical action of radium rays, says that radium and uranium rays act upon silver gelatino-bromide, but produce no effect upon Daguerre plates, or upon photographic papers, and says that colorations of glass, porcelain, paper and certain crystals, as well as the painful physiological effects also belong to this class of phenomena., He also calls attention to the transformation of white into red phosphorus in 24 hours, the reduction of mercuric chloride in the presence of oxalic acid with the precipitation of calomel, and finally the destruction of the germination power of seeds after long exposure.

Becquerel also shows that radium rays possess the same power as the electric spark, or the prolonged action of violet or ultra-violet rays, of restoring the phosphorescent properties under exposure to heat of a body deprived of them by over-heating.

Practically all the radium which has thus far reached this country, with the exception of that in the possession of the author, has been the German radium, and Prof. Curie tells the writer that he had tested all of the German productions, and he has found none of them to exceed a radioactivity of 300.

De Haen of Seelze near Hanover, Germany, and Giesel, of Brunswick, also have manufactured radium. De Haen recently informed the writer that the preparations he puts on the market cost ten and thirty shillings per gramme.

As indicative of the enormous difficulties to be encountered in procuring this wonderful substance, it is interesting to note that it takes 5,000 tons of uranium residues to produce a kilo (2.2 pounds) of radium; and the cost of handling these residues is $2,000 per ton. To secure the chemically pure radium is enormously expensive, and it would be impossible to do this by chemical analysis, therefore the far more sensitive electrical method is employed, and the Curies say that they can detect the presence

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of a radioactive substance by the means of such a minute quantity that it would require 5,000 times this amount to show at all in the spectroscope. And it is stated that this method of electrical analysis is thousands of times more sensitive than spectrum analysis and millions of times more sensitive than chemical analysis.

In Fig. 4 is shown the "electrometer" method with which the Curies have studied the radioactivity of different substances. It consists of two plates, A and B, on the latter of which is placed the radioactive substance to be tested. This makes the air a conductor of electricity between the two plates, and for measuring this degree of conductibility, the plate B is brought to a high potential by connecting it to one side of the storage battery P, the

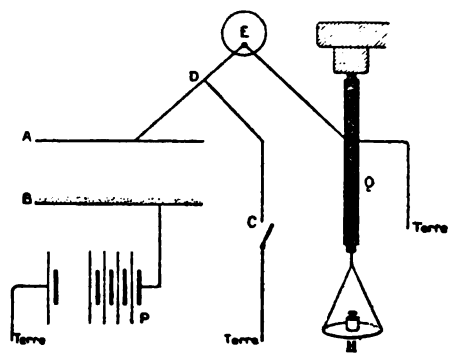

FIG. 4.—Apparatus employed by M. and Mme. Curie in the study of radioactivity.

other side of which is connected to the ground. If the plate A is brought to the potential of the ground by the wire C-D, an electric current begins to flow between the two plates, A and B. The potential of plate A is shown by the electrometer E. If we cut this communication with the ground at C, the plate A becomes charged causing the electrometer to deviate. The speed deviation is proportionate to the intensity of the current and can serve for measuring it. But it is preferable to make this measurement by compensating the charge taken by plate A, so that the electrometer remains at zero. The charges which are extremely feeble can be compensated by means of a Piezo-electric quartz Q,

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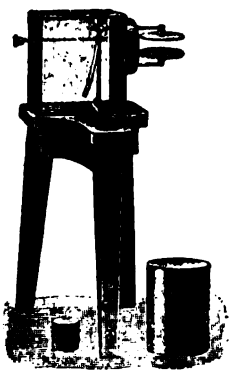
one armature of which is connected with the plate A, and the other armature grounded. The quartz plate is given a certain tension by weights placed on the plate H. This tension is gradually produced and gives a charge of a definite quantity of electricity which can be measured. The operation may be so regulated that there is a constant compensation between the quantity of electricity which passes through the condenser and that of the opposite sign furnished by the quartz. So we can measure in an absolute value the quantity of electricity passing through the condenser in a certain time.

Doubtless some loss is caused by the rays which pass directly through the condenser plates.



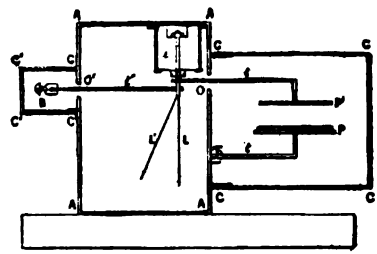


FIG. 5.—Curie's Electroscope for the study of Radio-activity

Dolezalek has designed a very sensitive type of electrometer built by Bartels of Göttingen, a description of which may be found in *Verk, der Deutsche Physik Ges., iii* (1901).

It is well known that the leaves of a gold or aluminum foil electroscope will hold their charge in dry air indefinitely; but the Becquerel rays are found to dissipate the charge by ionization of the air, or rendering the air a conductor of electricity (the electroscope may also be discharged by Roentgen rays, cathode rays and ultra-violet light).

In Fig. 5 is show a form of electroscope devised by the Curies for the study of radioactive substances. Referring to the diagram to the right, it will be noted that the electroscope consists of a single movable sheet of gold or aluminum foil attached to a stationary sheet of copper L, being supported by the insulating

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piece I. The radioactive substance to be tested is placed on the lower of the disks P and P′, preferably on a removable plate. The radiations make the air a conductor between these two plates The electroscope is charged by means of a stick of ebonite rubbed briskly and placed near the rod B. This deflects the sheet L′, from the vertical and it so remains for a very long time. When radioactive substances are brought near it, the gold or aluminum leaf is caused to lose its charge, and the leakage is observed by means of a stationary telescope shown in the left hand figure, which is provided with a micrometer scale. The time taken for the discharge of the electroscope is taken by means of a chronometer or watch. By suitable lighting, the front edge of the foil may be made to appear as a very fine line, and its position noted with great precision.

By examining the diagram it will be noted that the upper condenser plate is connected with the metallic case. Detachable metal cases are placed over the condenser plates and over the rod for charging the electroscope. Two of the sides of the case are of glass.

I have here a simple form of electroscope with leaves of aluminum foil, which serves to show the ionization of the air; when the radium is brought near the divergent leaves lose their charge of negative electricity and rapidly come together.

It is of paramount importance that the radioactive substance should be kept in a room distant from the electroscope.

At the present moment the clothes of every person in this room and all the walls of the room are radioactive by reason of the presence of the nine preparations of radium which I have here this evening.

Prof. Curie told the writer that it was often impossible for him to go near his instruments to make any measurements for hours, after being in the proximity of some radium, and those who have worked with this substance have found the greatest difficulty in keeping their tools and instruments and themselves free from the radioactivity imparted by the radium. The energy represented by radium is something enormous.

Elster and Geitel* have shown that a fine wire of any metal placed in the atmosphere and charged negatively from some source of current, say of 500 volts, causes the wire itself to become radioactive, and this radioactivity may be scraped off

* *Phys Zeit.*, 1901, ii., p. 590

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and will affect photograph plates, ionize the air, etc. It cannot, however, be washed off. It is stated that lightning rods and even the leaves of trees all become radioactive and it has been shown that falling rain and snow are for a time quite powerfully radioactive; and after they have fallen, a wire negatively electrified in the atmosphere has only a small amount of radioactivity, apparently showing that the rain and snow have carried the radioactive particles in the atmosphere down to the ground.

McLennan has made experiments with the negatively charged wire in Montreal and subsequently at the foot of Niagara Falls; and has found the result about one-sixth as powerful in the latter place as in the former; and he has also shown that it was not necessary to electrify the wire used at Niagara Falls, as it received a sufficient charge from the electricity in the atmosphere.

McLennan found that rain caught in a vessel and immediately evaporated to dryness imparted radioactivity to the vessel in which it was evaporated.

Ordinary water when evaporated and rain water which has stood for several hours before being boiled down do not yield any radioactivity.

As an evidence of radioactivity imparted to another substance by radium, I have here some pieces of cardboard which constituted the box which held my samples of radium for several months. The box becoming injured, I broke it up, fortunately saving the pieces; and six days after the radium had been removed, I looked up the pieces and was surprised to find them luminous in the dark. Subsequently I tried their effect on a photograph plate; but did not succeed in getting any impression. Three weeks later it occurred to me to try and stimulate the radioactivity of the cardboard, which had not been near radium for over a month, by burning magnesium wire, when I found I could make the cardboard brighter than it had been in the first place. I have also stimulated the radioactivity by sparks from a coil, especially when producing ultra-violet rays, by using a condenser bridged across the secondary and employing pure iron electrodes. I tried the burning magnesium with various samples of cardboard which had not been exposed to the radium, and there was no phosphorescence. It has already been stated that various substances which become radioactive retain that property for a short time only, and it is interesting to note its retention for such a long period of time and to note this

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ability to stimulate and make visible the imparted radioactivity.

This experiment suggests the discovery made by Prof. E. Wiedemann that a mixture of sulphide of calcium with a little sulphate of manganese is not altered when exposed to cathode rays; but some time after its exposure it bursts into a vivid greenish glow when slightly heated; and to this phenomenon he has given the name " thermo-luminescence."

Prof. S. P. Thompson also showed that fluorspar which by prolonged heating has lost its luminescing power, regains the power of thermo-luminescence on exposure to Roentgen rays when reheated.

Prof. Trowbridge also finds that this restoration is also effected by exposure to the electric glow discharge, but not by exposure to ultra-violet light.

It is also stated that an object coated with calcium sulphide and exposed to the sunlight will phosphoresce about ten hours; and even after it has lost its luminosity, it can be caused to again give light by heating first by the hand, then over a water bath, and finally on a hot stove.

McLennan has found a very large number of salts are brought into a condition by cathode rays, in which warming makes them radioactive for a short time, the supply of negatively charged particles discharged from the surface coming to an end.

Prof. Rutherford of Montreal, who has given a great deal of attention to radioactive substances, particularly to investigations into thorium, which next to radium is the most radioactive substance yet discovered, has found that by electrifying a wire negatively with a current of 500 volts connecting the positive pole to the ground; and by connecting a sample of thorium to the earth, that the thorium particles were attracted to the negatively charged wire, producing a greater radio-activity than he had ever found in any thorium preparation which he had made.

I have here a sample of oxide of thorium, the radioactivity of which was discovered independently by Schmidt and Curie. This sample is between 98 and 99 per cent. purity. From this body Prof. Rutherford has isolated a substance which he calls " ThX;" and extraordinary as it may seem, it has been found after separation of the active constituents represented by the ThX from the thorium, that the ThX loses its radioactivity, and this is taken up by the thorium in exactly the amount which the other loses.

Sir William Crookes has also separated a non-uranium residue

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from uranium, leaving the latter without radioactivity. Whilst the whole of the radioactivity has been concentrated in the residue to which the name UrX was given, Crookes, as already stated, claims that Actinium is but another name for his UrX.

The only case of radioactivity induced by cathode rays in a neutral substance has been that of bismuth, discovered by Villari.

Prof. Curie has discovered that radioactive gas emanates from radium, and Rutherford has discovered the gaseous emanations from thorium, Messrs. Rutherford and Soddy have investigated extensively these emanations, and they have succeeded in condensing them at the temperature of liquid air. A preliminary account appears in the proceedings of the Chemical Society of London for December, and Prof. Rutherford writes me that the full paper will shortly appear in the Philosophical Magazine; and he states furthermore that in his opinion this proves bevond doubt the gaseous nature of the emanations.

The serious physiological effects of radium are well known, and Messrs. Giesel, Becquerel, the Curies and others, have given important evidence thereof. As stated in the appendix of a paper read by the writer at the 159th meeting of the INSTITUTE on January 3, 1902, dealing with the subject of radioactivity, Prof. Curie told the writer that he would not care to trust himself in a room with a kilo of pure radium, as it would burn all the skin off his body, destroy his eyesight and probably kill him. The writer felt the effects for weeks of a slight burn from inadvertently carrying a wooden box containing eight tiny sealed glass tubes of radium under his arm for several hours.

Mr. W. E. Hidden has called the attention of the writer to some phenomena which he has observed in a mine in Barringer's Hill, Llano County, Texas, which mine contains yttrium, thorium and uranium. Pockets of ore have been found, ranging from a few ounces up to a capacity of 70 kilos, which were the nuclei or focal points of rigid lines radiating in every possible direction. These lines penetrating great masses of quartz and orthoclase feldspar, and gigantic pegmatyt, to distance often of several feet, in some cases of from five to eight feet, he has observed that these radial lines were fissures and bore no relation to the natural cleavage or the crystalline form of the huge rock masses in which they existed. Easy parting took place along these radial lines, making the ore quickly available.

It is Mr. Hidden's theory that, as these lines directed to ores

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rich in uranium and thorium, both well known sources of radium. etc., the phenomenon is due to an electric or other effect of radio-activity; it being untenable, he believes, to explain this phenomenon on the basis of expansion or contraction.

The slide which I will show on the screen shows clearly a pocket of ore with the lines radiating therefrom in all directions.

Eighteen years ago, while in Italy, the author visited the celebrated aquarium in Naples, which is probably the finest in the world; and while there was enabled to test the shocking abilities of the Electric Ray, or " Torpedo Galvani " and was astonished at the tremendous shock which he received; and in this connection, it is interesting to call attention to the fact that there are fifty or more fishes which are known to possess this property of giving powerful shocks. The " Gymnotus " or Electric Eel, and the " Torpedo Galvani " or Electric Ray being the best known of these.

It will be recollected that Faraday drew a powerful spark from a Gymnotus at the Polytechnicum, London, and he estimated the shock to be equivalent to that given by a battery of leyden jars of 3,500 square inches of surface. And many writers have referred to the ability of these electric fishes to give powerful shock for a long period of time. D'Arsonval has caused them to light incandescent lamps and they have been known to magnetize needles and decompose water by the electricity they produce. These fishes doubtless using this faculty as a means of defence and also for procuring food. My object in mentioning this is to state that last Fall I again visited Naples and thinking that perhaps an electric torpedo was on exhibition, it occurred to me to take with me some half dozen tubes of radium which I had in my bag, and see whether the radium had any effect upon the power of the fish to give powerful shocks. The fish, as at the time of my previous visit, was lying in a shallow wooden box containing wet sand and a small amount of water. By taking hold of the side of the fish and pressing with the thumb on one side and the fingers on the other, or by either pinching or tapping the fish, the cells with which the fish was equipped discharged themselves and gave a shock sufficient to twist one's arm very badly. After the members of our party had each received a shock, and as soon as a few persons present had gone away, I laid the six tubes of radium on the fish (which is shaped very much like a flounder), leaving them there for about twenty minutes. I then replaced the tubes in the box, and taking hold

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of the fish tried for fifteen minutes to get it to give me a shock by tapping or pinching in the same manner as previously done when the fish gave off shocks, and without receiving the slightest shock. Now, I am prepared to admit that the fish might have been "entirely out of shocks"; still, it is well known that these fishes will continue to give out shocks for a very long period of time, one authority reporting 360 shocks in seven minutes' time; but after exposing the fish to the radium, I could get absolutely no manifestation; and in this connection, it is to be remembered that the physiological effects of radium, such as burning, destroying microbic life, producing the sensation of light when a tube is held against the closed eye or temples (which is doubtless largely due to the phosphorescence of the pupil of the eye, but which may also affect the nerve centers), and also the electrical effects, where charged bodies are caused to give off their charge by the ionization of the air; and one must also remember the very numerous chemical effects and the destruction of the germinating power of seeds, the changing of oxygen into ozone, and various other phenomena of radium which would lead one to wonder whether the radium did not affect the ability of the fish to give off electric shocks, perhaps producing a partial paralysis.

The experiment is of some interest, and may be perhaps repeated by others who have better facilities than I to continue the investigation. I have sometimes wondered how that fish was getting along in Naples; though I believe the waters of the Mediterranean abound in them.

Note—Since writing the above description of his own experiments, the writer has learned of the recent experiments conducted by Prof. Curie, in which a few milligrams of radium introduced beneath the skin of a mouse near the vertebral column produced death by paralysis in three hours; and tubes of radium placed in contact with the back of the necks of guinea pigs have killed or paralyzed these animals in a few hours, according to the length of exposure to its fatal radiations.

As illustrating the action of radium rays upon bacteria, E. Aschkinass and W. Caspari speak of exposing cultures of *micrococus prodigiosus* to a radium preparation, and state that the rays killed the germs very effectively in about three hours.

The work of Rutherford, the Curies, Becquerel and others has demonstrated that there are three entirely distinct types of rays emanating from radium (Rutherford having first pointed out that uranium possessed two separate types of rays, "α" and "β."

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the former easily absorbed even by gases, whilst the latter are very penetrating and but little absorbed by gas). Those which constitute by far the most important class are the "α" rays. They constitute the major proportion of the rays, and are those which produce the greatest portion of the ionization of the gas, which has been observed under experimental conditions.

These "α" rays possess in common certain characteristics of Roentgen rays, and by many have been thought to be Roentgen rays. I shall call your attention later to certain effects which are identical with those produced by Roentgen or X-rays. They have been considered absolutely non-deviable, as X-rays have been held to be.

Rutherford has, however, recently shown that in a very powerful magnetic field he could deflect about 30 per cent. of the rays, and in experiments now being conducted with a strong electric field, he has been able to deflect about 45 per cent. of the "α" rays. The "α" rays are readily absorbed, and a thin screen of metal will serve to cut off the greater portion of them.

In this connection I would state that Mr. Tesla informed the writer recently of an experiment he had made in which he had succeeded in deflecting the X-rays themselves, and M. Blondelot has recently claimed as the result of his experiments that X-rays are susceptible of polarization. If this is so, it is argued they may be shown to be ordinary light waves of extremely short wave length.

Strutt and Crookes have suggested that the "α" rays consist of positively electrified particles, and this view Rutherford supports, calling attention to the fact that they possess characteristics similar to the "Canal Strahlen" of Goldstein. These Goldstein rays have been shown by Wien to be positively charged particles, moving at high velocities.

Rutherford, as a result of his most recent observations, considers that the "α" rays move at much higher velocity than the Goldstein rays; and he estimates that the energy of the "α" rays is a thousand times greater than that of the "β" rays.

Rutherford says all the radioactive substances, including polonium, as well as excited bodies and the emanations, give out "α" rays.

The "β" rays are much more penetrative and much longer, and in every particular correspond to the characteristics of cathode rays. They are readily deflected by a magnet. They

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discharge electrified bodies by ionization of the air, affect photograph plates, etc.

M. Villard, in 1899, proved that the cathode rays are negatively electrified corpuscles or fragments of atomic hydrogen, and these corpuscles, as they were named by J. J. Thomson, which he has shown to be one one-thousandth of the mass of the hydrogen atom, are projected from the cathode at a speed approximating 70,000 miles per second.

The " γ " rays are the rays possessing the greatest penetrative effect. They will excite or produce radioactivity through the air at a distance of three or four feet or more.

Some recent experiments made by Rutherford show the relative penetration of the three classes of rays through aluminum sheets of varying thicknesses, before a loss is observed of half of the intensity, and this shows for the

" α " rays a thickness of aluminum of .0005 cm.
" β " rays a thickness of aluminum of .05 cm.
" γ " rays a thickness of aluminum of 8. cm.

Mr. Rutherford, who has conducted most painstaking investigations into the penetrative character of the radiations from uranium, radium, thorium, etc., recently wrote the author in answer to some questions on the subject, that he had found that the radium rays were reduced to half value after passing through 1 cm. of lead, 1 inch of iron and about 8 inches of water, the radiation being reduced to about 1 per cent. of its original value, after passing through 7 cm. of lead, 7 inches of iron and 56 inches of water.

In the lantern slide thrown on the screen is an interesting illustration of the effect of magnetism on the deflectable rays from radium. There are four large steel magnets, two being placed opposed to each other, and the other two so that unlike poles are opposite to each other, making a strong field of force between the two magnets. I have placed six tubes of radium a short distance above the magnets and in a line running across and between the poles of the two pairs of magnets. It will be seen that the magnetic rays in the case of one pair of magnets have repelled the radium rays so that the negative is but slightly affected. Whereas, in the case of the other pair of magnets the radium rays have been attracted by the magnets affecting considerably the negative around the pole pieces.

Prof. Curie states that half of the induced radioactivity, when exposed to the air, is lost in certain substances in half an hour;

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but in a closed vessel, where the air has been made radioactive. however, this radioactivity has not lost half of its strength, even after four days' time.

It is desirable to keep radium free from moisture, preferably in sealed glass tubes. It readily takes up moisture, and then soon loses its luminosity, which may, however, be regained by dissolving and precipitating the substance and thoroughly drying it. The luminosity may also be considerably heightened by subjecting the radium to high temperatures.

Polonium like uranium does not possess the power of exciting radioactivity, as it does not give off any emanations; whereas, in the case of radium and thorium, there is an actual emanation, producing radioactivity in surrounding objects by the deposit of radioactive matter.

When one considers the remarkable effects produced by radium it would almost seem that it is matter tearing itself into tiny pieces, and projecting these infinitesimally small particles through all matter at a speed from half to even the full speed of light, and rendering all substances about it radioactive, and still without appreciable loss in weight in the original substance, and without disparagement of the accepted wave theory of light. one naturally " harks back " to Newton's corpuscular theory of light.

While various theories have been advanced to account for the phenomena of radium, there remain many things which have not been satisfactorily accounted for; and perhaps the subject which has been most widely discussed is the loss in weight of radio-active substances.

At the British Association meeting last summer, Prof. J. J. Thomson is reported to have stated that if a square centimeter of surface were covered with pure radium, it would only lose in weight one thousandth of a milligram in a million years. This is in accordance with the previous statements made by Becquerel.

Later in the year, A. Heydweiller, of the Royal University, Munster, Germany, stated that he had been testing a sample of De Haën's preparation of radium, and found that it lost in weight two one-hundredths of a milligram per day for fifty days, and a whole milligram in that period. (*Phys, Zeit*, Oct. 15, 1902.)

The great discrepancy in the statements on this important subject, led the writer to enter into correspondence with Profs. J. J. Thomson, Henri Becquerel, Lord Kelvin, Sir William Crookes, P. Curie and A. Heydweiller, which resulted in the following expression of views.

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Prof. Thomson was inclined to think that from the magnitude of loss found by Heydweiller, it must be due to some secondary effect, and he stated that he could not speak with certainty without a greater knowledge of the details of the experiments. As accounting for the results he, however, drew attention to the well-known coloration of glass by radium, by remarking, " One point, however, that ought to be attended to in these experiments is the effect of the radiation from radium on glass. Glass, as is well known, gets deeply colored when in contact with radium. It seems to me possible that the glass might be charged right through. If this were the case, it is possible that reactions might occur between the glass and the air, producing volatile substances and a loss of weight. I only throw this out with hesitation, for as I said before, I am not familiar with the details of the experiments."

Prof. Becquerel informed the writer that he knew nothing reliable regarding the experiments of Heydweiller, and called attention to his original paper on this subject which appeared in the *Comptes rendus* of March 26, 1900, adding, " I believe I am the first to have published an estimate in this way which could only result from my own experiments. The loss of one milligram per square centimeter requires one thousand million years. This statement refers only to the part of the deviable portion of the radiation to which measurements were applied; but this is only a part of the total loss. The deviable radiations comprise rays ranging from 10^9 and 3.10^{10} c.m Besides, there is also all the non-deviable portion, either penetrating or absorbing, which corresponds to a notable loss of energy; and in addition, if the emanation is of material importance, which seems quite probable, the loss on this account would be a thousand times greater. These estimates are but theoretical, for it is probable that at least a portion of the mass calculated or estimated as material is apparent and corresponds to the effects of induction."

In response to an expression of view from Sir William Crookes on a theory to satisfactorily account for the phenomena of radioactive substances, he wrote as follows: " You will find them fully given in my address to the British Association at their Bristol meeting in 1898. I have not seen any special reason to alter the views there propounded "; and in writing on the subject of Heydweiller's experiments, Prof. Crookes says, " I do not think the experiments of Heydweiller have been corroborated by other observers; and there are many sources of error in his

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experiments which I should like to see discussed before giving credence to it. Personally, I find no loss of weight in a rich sample of radium compound during continuous weighings extending over many months. I should be inclined to agree with Becquerel and J. J. Thomson."

Lord Kelvin wrote that he was sorry not to have been able to make any experiments on radioactive substances which could allow him to offer any opinion that would be helpful on the subject, and added, "What you tell me regarding radium and your correspondence with Prof. J. J. Thomson is very interesting."

On this point Prof. Curie recently wrote me as follows: "I never did believe in the exactness of Mr. Heydweiller's experiments; and I always thought he did not take care enough to avoid some source of errors. In fact, with a substance considerably stronger than his own I only obtained a reduction in weight of 1-10 of a milligram in four months for several decigrams of substance, and as the tubes were used at the same time in several experiments, that loss of weight does not allow me to affirm that radium is losing weight spontaneously. I believe, meanwhile, as does Mr. Heydweiller, that the question cannot be answered in any other than an experimental way, and that all speculative theories are of small interest. I have published my recent researches in the *Comptes Rendus de l'Acadamie des Sciences de Paris*."

As regards the published statements of Prof. Heydweiller's experiments, the writer can state that he is most reliably informed that a mishap occurred during his experiments which resulted in one of the tubes becoming cracked, which was not observed until later; and that this practically nullified the results published; and, in fact, they have not been confirmed by subsequent tests; but, on the other hand, they tend to corroborate the experiments of Becquerel and the statements made by him, Sir William Crookes, J. J. Thomson and others. The writer is also informed that Prof. Heydweiller is continuing further experiments, the results of which will doubtless be published when his investigations are complete.

As bearing upon the coloration of glass already referred to, I hold in my hand a flask which I secured at the laboratory in Paris, which has contained radium, and has been most beautifully colored a deep violet. I also have several tubes in which radium has been kept, which are similarly colored, and in this connection I would call attention to the fact that X-ray tubes which have

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been in use for a considerable time become similarly colored, forming another link between the Roentgen rays and radium rays.

I also have here a tiny bulb of glass which is colored a deep brown. I have seen only one other piece of glass colored in this way, this being due to the difference in the chemical constituents of the glass (though in some cases the glass subsequently turns a violet color). This is a duplicate of the tiny tube which Prof. Curie showed the writer, which contained between two and three one-hundredths of a gramme of chemically pure radium.

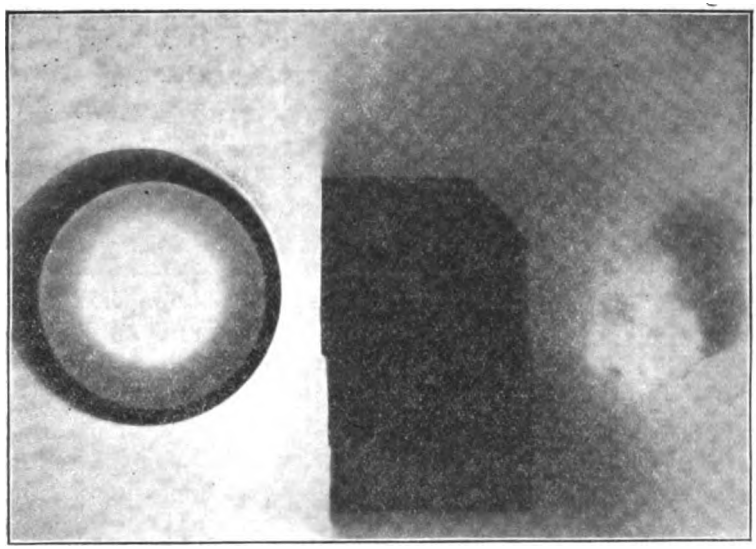

FIG. 6.—Radiograph Made by Radium of a Disc for Testing Radioactivity, a Block of Rock-salt and a Lump of Pitch-blende.

It is interesting to note that the Becquerel rays induce activity which persists, whereas that excited by Roentgen rays ceases immediately on the removal of the rays.

As illustrating the X-ray character of radium rays I would call your attention to Fig. 6, in the center of which is shown a block of rock salt. The original sample was about one inch thick, and was so transparent that a person's features might be seen through it. The rock salt is not only transparent to ordinary light, but also to ultra-violet light, whereas it is very opaque to X-rays.

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Mrs. Hammer, appreciating the series physiological effects of radium, has made the interesting suggestion that radium be kept in boxes made of rock salt; and the author is now having such a receptacle made. This might be even more satisfactory than a lead box. It would be interesting to note the change in the temperature of such a box or vial which so well intercepts the Radium rays.

The illustration referred to was made by placing the rock salt on a photograph plate with the radium some 5 inches above it.

To the right of the rock salt is shown a piece of uraninite (pitchblende), from which radium is extracted; and you will note that not only has the mineral been photographed by the radium above it, but the radium has acted on the radioactive constituents of the pitchblende and caused this to affect the plate.

The disk shown at the left of the cut is one made in Paris for the examination of radioactive substances. I have one of these here, and it consists of a rim of brass, enclosing a brass washer with a glass disk at the center. The opposite face is covered with aluminum foil, and between the aluminum and the glass is placed some radium of 1,000 radioactivity. Substances which it is desired to examine are laid on this disk. It is, however, a rather crude piece of apparatus; but in the cut shown not only has the disk been photographed by the radium 5 inches above it, but the radium inside of the disk has penetrated through the aluminum and fogged the plate.

In Fig. 7 are shown some interesting effects of the radium rays in affecting a photograph negative after passing through lenses. The lenses "A" and "B" are plano-convex condensing lenses, one being placed with the flat surface down, and the other with the convex surface down. "C" is a double convex lens of crystal, "D" is a plano-convex lens of uranium glass and "E" represents an ordinary glass prism.

It is stated that radium rays cannot be reflected, refracted or polarized. Those familiar with the phenomena of light will, I feel sure, be interested in the above photograph.

In Fig. 8 is shown another illustration of the penetrative character of the rays, it being a thick lead box containing six tubes of radium, ranging from a radioactivity of 40 to 7,000; this box being laid upon a large steel magnet ⅛ of an inch thick. You will note the degree of penetration of both the lead and the steel varies according to the radioactivity of the radium in the various tubes. The exposure was made in twenty-two hours.

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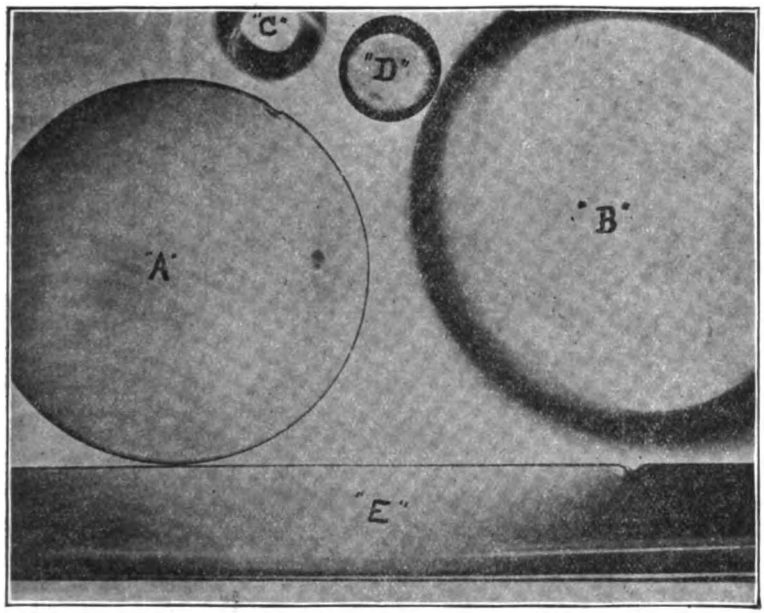

FIG. 7. Radiographs of Various Types of Lenses Made by Radium.

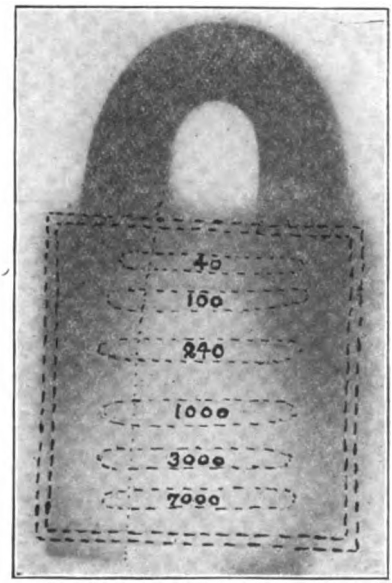

FIG. 8.—Radiograph showing Degrees of Penetration of a thick sheet of Lead and a Steel Magnet by Tubes of Radium of Different Radioactivities.

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Fig. 9 illustrates the penetration of the rays through black paper, the steel tool shown having been laid on the plate covered with two thicknesses of heavy black paper, such as used for

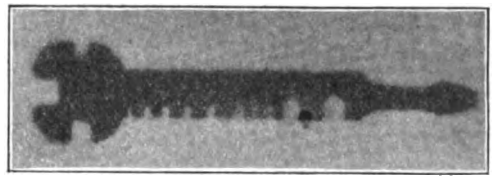

FIG 9.—Radiograph of Steel Tool made by Radium Acting Through Two Thick X-ray Plate Envelopes.

wrapping X-ray plates; a single sheet of which is entirely impervious to light. The exposure was made in twenty-four hours.

Fig. 10 shows a mouse which was radiographed in twenty-four hours by laying it directly on a plate, which was, as in the case of

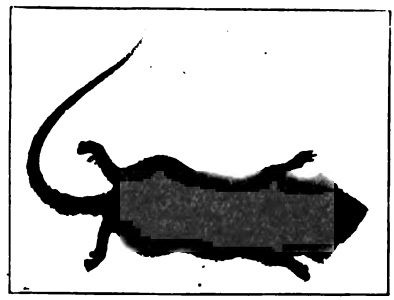

FIG. 10.—Radiograph of a Mouse Made by Radium in Twenty-four Hours.

other experiments, placed in the bottom of a trunk, the trays being replaced and the trunk wrapped in three thick rugs, and kept in a dark room for twenty-four hours.

The radiograph of the mouse shown in Fig. 11 represents a mouse caught on another occasion, in which I placed the mouse, trap and all on the plate, leaving it there for three days. The trap was an ordinary 6 cent trap; and it will be noted that the metal parts of the trap are shown opaque, whereas the portion of the wood nearest to the radium is shown absolutely transparent, as if it had been exposed to X-rays. In the original photograph

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the mouse is also shown somewhat transparent, indicating slightly the bones.

I also show you in Fig. 12 and upon the screen a slide which I have made of a radiograph of a human hand. This was exposed for eight days, and bears resemblance to an X-ray picture which has been overexposed. In making a faint print of this, a slight trace of the bones is shown and the embalming material employed is brought out strongly. This is, perhaps, the first picture made of the human hand by means of radium and it would not have been possible, of course, to have exposed a living person to these rays for even a small percentage of this length

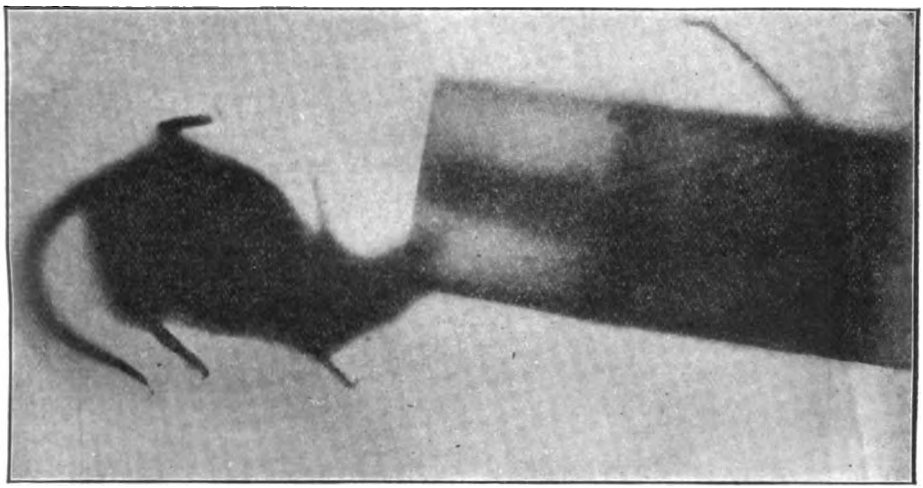

FIG. 11.—Radiograph of Mouse Caught in Trap and Exposed to Tube of Radium for Three Days. (Note Transparency of Wood, as with X-rays).

of time. Perhaps subsequent experiments will bring out much more strongly the bone structure (the irregularity in the fingers is due to their being somewhat cramped).

As X-rays will excite phosphorescence in many substances, one would naturally wonder whether there were any X-ray characteristics in phosphorescent substances.

An interesting experiment is shown in Figs. 13 and 14. In the former experiment, I have placed strips of various metals, such as brass, iron, copper, tin, lead, tin foil, aluminum, platinum, magnesium, etc. and strips of carbon, vulcanite, glass, mica and celluloid.

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FIG. 12.—Radiograph of a human hand made by Radium in 8 days' time.

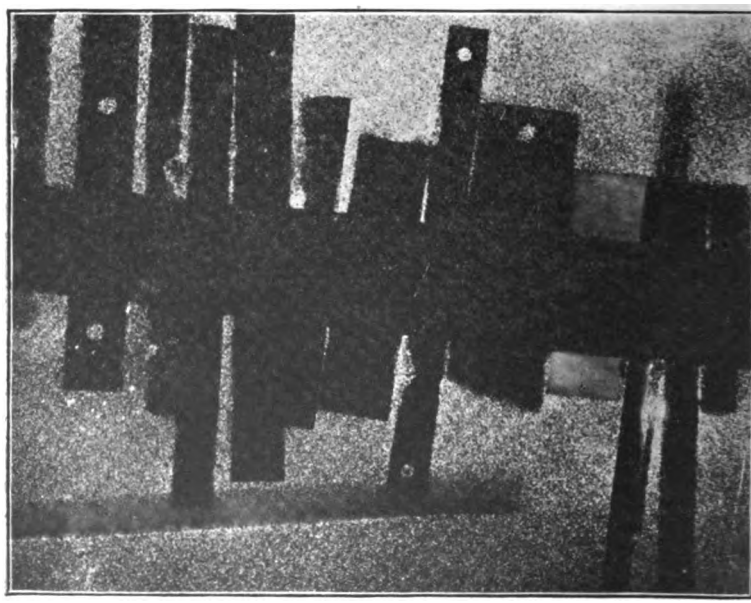

FIG. 13.—Photograph Made by Phosphorescent Sulphide of Calcium of Iron, Brass, Copper, Tin, Lead, Aluminum, Platinum, Tinfoil, Magnesium, Carbon, Glass, Mica, Celluloid, Vulcanite, etc., and Strip of Black Paper. (See Fig. 14.)

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Across the middle of the plate I have placed a strip of thick black paper cut from an X-ray plate envelope. I then sprinkled over the entire plate by means of a sieve sulphide of calcium, which I had made brilliantly phosphorescent by exposure to burning magnesium ribbon. The only substances which allowed the light to pass through at all were the glass, mica and celluloid, the other substances, including the paper, being very opaque, showing apparently only the presence of ordinary light rays. This plate was placed for twenty-four hours in a dark room.

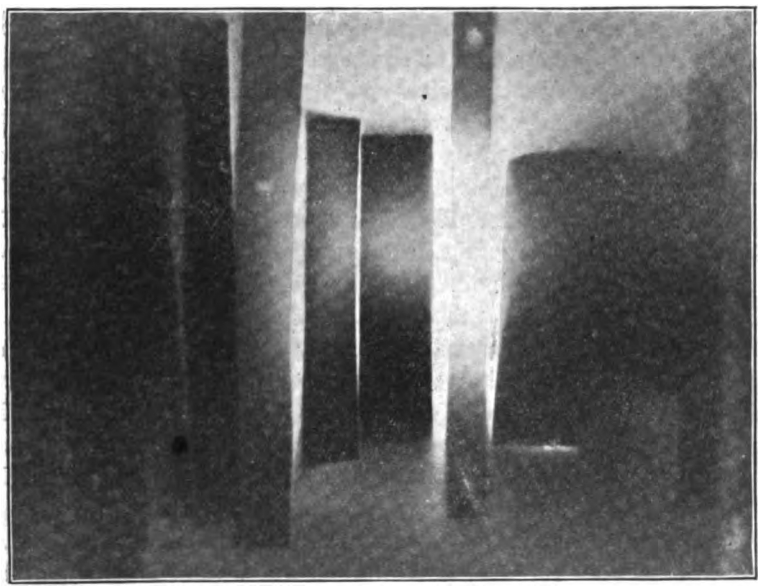

FIG. 14.—Radiograph Made by Radium of Same Substances as in Fig. 9. Note Black Paper is Transparent, as are Certain of the Other Substances especially those directly below the Radium.

In Fig. 14 are shown some substances similarly arranged, but exposed to a tiny tube of radium of 7,000 radioactivity, which was placed 3 inches above the plate and near the center. The exposure was made for twenty-five hours; and it will be noted that the strip of black paper has entirely disappeared, and the various substances underneath it have been penetrated to a greater or less degree; particularly, those nearest to the radium.

A bibliography of "Radio-Activity," even at this early date,

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would be very extensive; among the publications containing the most important contributions are *The Phil. Mag., Comptes Rendus, Ann. der Physik, Revue Gen. des Sciences, Nature, Jour. de Phys., Soc. Francaise Phys. Bulletin, Chem. News, Phys. Ges. Verk., Phys. Zeit, Science Abstracts, Wied, Ann., Proc. Royal Soc., etc.*

The Properties and Applications of Selenium.

The extraordinary property which selenium possesses of varying its electrical resistance on exposure to light is a phenomenon which has been known for a long time; but the commercial applications of this peculiar property possessed by selenium have not been properly appreciated up to the present time.

It is my purpose to invite your attention this evening to a number of applications of selenium which the writer believes will prove of no small interest to the electrical engineering profession, and perhaps stimulate investigations in this most promising field.

The Swedish scientist, Berzelius, discovered selenium in 1817, as a by-product from the distillation of sulphuric acid from iron pyrites. The proximity of the earth and moon suggested to Berzelius the name "Selenium" after the Greek "selene" (moon); this being the result also of the striking similarity of the properties of selenium with those of tellurium, which is a term derived from the Latin "Tellus," (earth.) Its atomic weight is 79.5; specific gravity when crystalized, 4.788 its observed vapor specific gravity at 2588° F. 5.68. It is a non-metallic element, which possesses characteristics similar to phosphorus, sulphur and tellurium. When melted at 212° Centigrade and allowed to cool rapidly, it forms a brown amorphous mass of conchoidal fracture. In this condition it is a high class insulator. It has been said that a small piece of it would represent the resistance of a wire stretched from the earth to the sun. When heated for quite a time at a temperature of 100° Centigrade, selenium becomes a conductor of electricity to a limited degree, this increasing with an increase of current and varying according to the direction. Selenium has neither taste nor smell.

The red vapor rising from selenium when subject to intense heat is exceedingly poisonous, and care should therefore be taken when experimenting with selenium in liquid form.

Selenium is usually supplied commercially in a vitreous form. Here are some samples of it, and you will note that it is as structureless as glass and resembles black sealing wax. I also

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have here some amorphous selenium in which form it is a finely divided brick red powder. This changes into vitreous selenium when exposed to a temperature of from 80° to 100° Centigrade. In order to obtain crystalline selenium, in which form it is useful for selenium cells, it must be kept as already stated at from 100° to 200° Centigrade for some time, the black mass being changed into a hard slate-colored metallic looking substance. In this form even the thinnest films are opaque to light, whereas in the vitreous form the film would be transparent and ruby red in color. I have some of these films here for your examination.

Selenium is to-day employed to a considerable extent for the coloration of glass.

In 1851 Hittorf first discovered the effects of temperature on selenium; but it was not until February 12, 1873, that Mr. Willoughby Smith sent a communication to President Latimer Clark, of the Society of Telegraph Engineers of London, calling attention to the effect of light in reducing the resistance of selenium. An assistant of Mr. Willoughby Smith, a Mr. May, who was a telegraph clerk at Valencia, called attention to the fact that some pencils of selenium which had been used to give a high resistance in connection with some of the cable testing work conducted by Mr. Willoughby Smith, showed a marked change in resistance when the sliding cover of the box which held the selenium was removed, and the selenium was exposed to sunlight. These selenium pencils varied in length from 5 to 10 centimeters, and were 1 to 1½ mm. in diameter; they were hermetically sealed in glass tubes with connecting wires of platinum at each end. Little credence was given to the original announcement; and it was only after Earl Ross verified this statement, and proved that the action was due solely to light, and showed the effects of the light of different portions of the spectrum, that it met with serious consideration. Since that time much work has been done in investigating the properties of selenium, especially by Messrs. Shelford Bidwell, J. W. Giltay, Lord Ross and Sale, Draper and Moss, Hittorf, Adams and Day, Ayrton and Perry, Sir W. C. Siemens, Werner Siemens, Mercadier, Fritts, Minchin, Ruhmer, Webb, Bell and Tainter, and many others.

Alexander Graham Bell some twenty years ago made some interesting experiments with his radiophone, a diagram of which is shown in Fig. 15, in which a mica or glass diaphragm covered with a silvered foil was used to reflect a powerful beam of light upon a selenium cell placed in the focus of a silvered reflector.

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To the selenium cell were connected a pair of telephones and a battery. At the back of the silvered diaphragm was a flexible tube and mouth piece into which words were spoken. The sound waves causing the diaphragm to vibrate sent pulsations of the reflected light upon the selenium cell, producing corresponding variations in its resistance and reproducing audible sounds in the telephone. Prof. Bell only used this over very short distances.

In 18 8 Prof. H. T. Simon of the University of Göttingen, discovered that an arc lamp, the circuit of which was in proximity to a telephone circuit, was caused to vibrate very perceptibly and he devised his interesting speaking arc by means of which he superimposed the sound waves produced by the telephone upon the circuit in which the arc was placed. He connected the lamp circuit with the secondary winding of an induction coil,

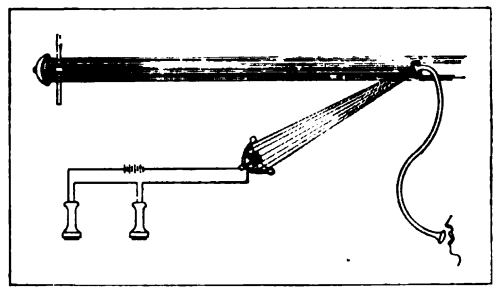

FIG. 15.—Prof. Bell's Radiophone.

the primary circuit being connected with the carbon transmitter, and a battery. The sounds thus produced originally were very weak; but by employing a suitable carbon microphone, the sound was reproduced to large audiences.

Conversely, the arc could also be used in conjunction with telephone receivers to receive sounds.

It is also found that the transmitter battery may be omitted, and a shunt taken from the arc circuit may be used with the transmitter and a suitable resistance. Again, this resistance may be displaced by storage batteries; and in this case to secure the most satisfactory results, self-induction (" reaction coils ") should be placed in the circuit of the arc lamp, allowing the direct current to pass without obstruction; but offering extremely high resistance to the alternating currents produced by the carbon transmitter. By compensating in this way any disadvantage in the use of the shunt is done away with.

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The transmitter may also be placed in shunt with the reaction coil instead of in shunt connection with the arc lamp, and this has the advantage that the rheostat used with the storage batteries may be omitted, provided the windings of the reaction coil are suitable for use as a resistance. By this arrangement, the lack of self-induction in the transmitter circuit permits of a very clear and distinct reproduction, sufficient to be heard by large audiences.

Mr. W. Duddell, of England, has made some most succesful talking arcs, which the writer had the privilege of seeing in London over two years ago. In his arrangement in the secondary circuit is placed a condenser, which prevents the lamp current entering the induction coil; but allows the induction current in the transmitter circuit to pass without obstruction; and this arrangement has the effect of greatly increasing the sound. By employing a condenser of from three to five microfarads, he compensates for the difference of phase produced by the self-induction in the circuit, thus producing the highest effect in the arc.

When Duddell uses the arc for transmitting sound waves, he employs in the shunt circuit to the arc a condenser and receiving telephone. It is advisable to employ as long an arc as possible. It has also been found that the Moore vacuum tube and the various types of mercury arc, such as Arons, Hewitt and Weintraub, are very suitable for this class of work, as well as the carbon arc; and where the latter is employed, either cored or treated carbons are advisable.

The theory advanced to account for the phenomena of the speaking arc, is that variations in temperature of the arc are produced by the variations of the current, and the change in the Joule effect produces a corresponding variation in the volume of the conductive gases in the arc.

The most successful and most extensive experiments which have been made with the speaking arc are those of Mr. Ernest Ruhmer, of Berlin, Germany, who has employed it in conjunction with his selenium cells for wireless telephony and with remarkable success. In Fig. 16 is shown the apparatus employed by Mr. Ruhmer, with which he has succeeded in transmitting speech over a beam of light 4½ miles in length*. Mr. Ruhmer's apparatus is shown in the illustrations thrown upon the screen,

* Mr. Ruhmer has recently written the author that he has succeeded in talking over a beam of light a distance of over ten miles.

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and in Fig. 17. In his experiments he employed an arc lamp with a flaring arc 6 to 10 mm. long, using an e.m.f. of 220 volts, the current varied from 4 to 5 amperes at 1 to 2 k.m., 8 to 10 amperes for 3 to 4 k.m., and 12 to 16 amperes for 5 to 7 k.m., and the resistance of his selenium cell was 120,000 ohms in the dark, this falling to 600 ohms in full sunlight. For the transmitting end, Mr. Ruhmer employs a carbon transmitter and a battery superimposing waves on the arc light circuit; and the beam of light is reflected to some distant point, where it is received by a parabolic reflector; in the focus of which is placed a selenium cell connected with a battery and a pair of very sensitive telephone receivers.

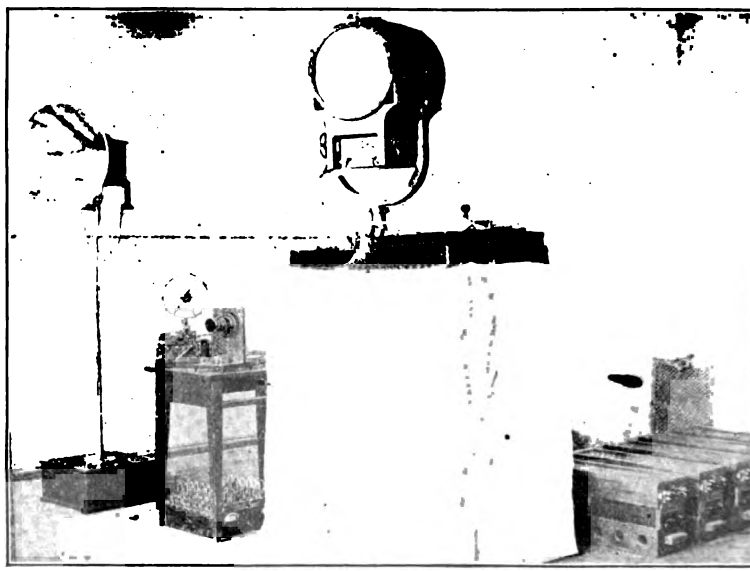

FIG. 16.—Ruhmer's Apparatus for Long Distance Telephony over a Beam of Light.

Mr. Ruhmer has conducted extensive experiments both by night and by day, and even during fog and rain on the Wannsee, near Berlin. On the screen you will see an illustration of his apparatus in actual work at night. (Fig. 17.)

Some time ago I suggested to Mr. Ruhmer the employment of Edison's tasimeter, the extraordinary sensitiveness of which is well known. He informed me that he had tried this; but had found it too " lazy "; and stated that he has secured most promising results by the employment of the thermopile; and with this he expects to be able to transmit sound over many miles.

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Mr. Ruhmer is about to commence extensive experiments under the direction of the German Government in connection with the Imperial fleet in the Baltic Sea.

Mr. Ruhmer has also suggested the employment of his photographophone, which I shall describe later, as a means of recording messages received at a distance.

Doubtless many present remember the interesting experiments made by Mr. Hayes at the Electrical Exhibition held in Madison Square Garden in May, 1899, in which music was transmitted over a beam of light. At one end of the garden was placed a telephone, before which a cornet was played, causing waves of

FIG. 17.—Ruhmer's Wireless Telephone Receiving Station at Wannsee, Berlin (taken at night).

current in the telephone circuit to be superimposed upon those in a neighboring arc light circuit. The light rays from this arc lamp were reflected across the Garden, where they were received in a parabolic reflector in the focus of which was a glass bulb containing filiments of carbon. This bulb was connected to a pair of ordinary phonograph listening tubes. The varying light which fell upon the carbon caused variations of temperature inside of the glass bulb which produced the original sounds in the listener's ear. A bulb simply coated with lamp black and containing nothing but air, would answer the purpose just as well.

Selenium cells may vary in resistance from 2,000 ohms to 500,000 ohms or more in the dark; and certain cells may be five

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to twenty times as good conductors of electricity in light as in the dark; and in the case of other cells, notably that of the Fritts' cell, which I have here this evening, and that of the Ruhmer cell used in his Wannsee experiments, will have two hundred times the conductivity in light that it has in the darkness; and the ratio may be even higher. They are usually made by winding carefully two separate lengths of wire, either of copper, brass, German silver or platinum, equidistant throughout their entire length upon such substances as slate, glass, mica or porcelain. The selenium is then spread thinly over the wires forming an insulation between the two windings. This form of cell was invented by Mr. Shelford Bidwell, F. R. S. No small amount of skill is necessary to wind these fine wires evenly and equidistant, and to cover successfully these wires with the selenium coating. One way of coating frequently employed is to warm the cell on a metal plate or sand bath heated by a Bunsen burner. When the stick of selenium laid on the plate shows evidence of melting, which takes place at about 120° Centigrade, it is drawn slowly over the wires, coating the same thinly and evenly. A steel spatula or a strip of mica can be used with advantage.

Or the strip of material on which the wires have been wound would be laid upon a brass plate covered by a strip of this mica, this being placed upon a tripod with a Bunsen burner underneath. Powdered vitreous selenium may thus be spread evenly over the wires, and the selenium will shortly melt; and where the portions of it crystallize, forming hard lumps, it will be necessary to continue the heating until these disappear. Then the selenium may be spread uniformly with a piece of steel, or better still, a strip of mica, care being taken to cover up the edges. Mr. Bidwell states that the temperature should be carefully regulated, as when it is too low hard crystalline lumps will form, and when too high the surface tension causes the selenium to form in drops, and it is then as difficult to spread as if it were mercury. The proper temperature should be only just above 217° Centigrade; and then the selenium is in a plastic semi-fluid condition and can be easily manipulated. When a satisfactory surface is secured, the cell should be placed upon a thick copper plate to cool quickly, when the selenium becomes black and lustrous. The Bunsen flame should then be turned down to give a temperature of about 120°, and the cell is then placed upon the hot plate; and shortly, the whole surface of these turns to a dull gray color. The temperature is then cautiously raised until signs of melting begin to

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appear, generally near one of the edges. When this occurs, the burner is instantly withdrawn and the flame lowered. The dark spot recrystallizes in the course of a few seconds, and the burner is then replaced and left for four or five hours, during which time the Se should be only a few degrees below the melting point. The coil should then be gradually cooled by lowering the flame gradually for an hour. This process of long heating and slow cooling is generally spoken of as " annealing."'

In Fig. 18 is shown an illustration of a number of types of selenium cells, including the Bidwell, Ruhmer, Giltay, Webb

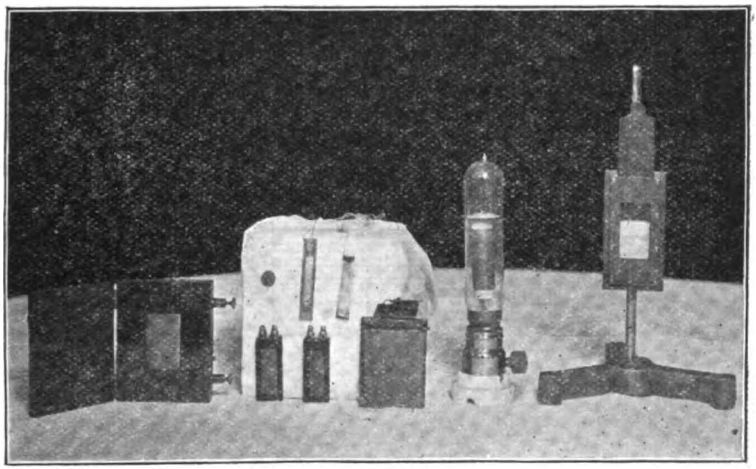

FIG. 18.—Types of Selenium Cells.

Clausen & Bronck, Mercadier and Fritts, which I have brought with me for your consideration.

The two cells to the extreme right and left are modifications of Mr. Shelford Bidwell's cells, the original form of which consisted of two fine copper wires wound side by side on oblong strips of mica with melted selenium spread over the surface, the one to the left being manufactured by Ernest Ruhmer, of Berlin, and by Messrs. Clausen and Bronck, which consists of copper wire wound on slate. The one to the right is manufactured by Mr. J. W. Giltay of Delft, Holland, and consists of platinum wire wound on slate and covered with selenium. The four tiny cells shown against the white background are made by Mr. Hartwell W.

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Webb, of New York City, and consist of German silver wire wound on slate. The cell to the right is placed in a sealed flat glass tube. The two lower Webb cells are incased in ebonite. The small round cell is a tiny Mercadier cell made by Mr. Webb. The method of making the Mercadier cell is to use two narrow ribbons of sheet brass or foil, separated by a ribbon of parchment paper rolled up like a spiral spring. This is held between wooden clamps, one surface being ground and polished off smoothly, and a thin layer of selenium being spread over it. An excellent idea of this cell may be had by noting Fig. 19, which shows the standard form.

In the center of the picture is shown a cell of Mr. C. E. Fritts, of New York City, for which I am indebted to my friend Prof. Geo. F. Barker. In the Fritts cell a very thin layer of selenium from one one-thousandth to one five-thousandth of an inch

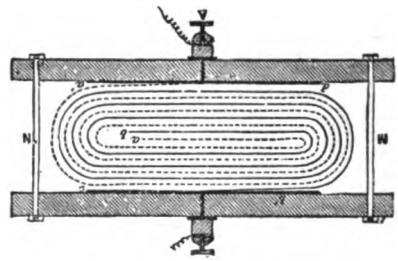

FIG. 19.—Mercadier's cell (block and dotted lines represent the two ribbons of brass).

in thickness is spread upon a plate of metal, generally zinc or brass. The selenium and metal plate form a chemical combination sufficient at least to cause the selenium to adhere and make good electrical connection. The upper surface of the selenium is then covered by a transparent conductor of electricity, preferably a thin film of gold leaf. Platinum or silver may also be employed. Thus the two surfaces of the selenium are covered by a metal and are connected to the two ends of the circuit. The upper or gold leaf surface, however, permits the light to pass through and affect the resistance of the selenium beneath.

The tall cell in the lamp socket shown is the latest form of Mr. Ruhmer's cell, and this type represents, I believe, the most important development which has been made in the selenium cell, and it has now become most stable and responds most rapidly to variations in illumination He employs two copper wires,

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wound spirally side by side around a cylinder of porcelain, which, after the wires have been covered with selenium, is placed inside of a globe, from which the air is exhausted and it is mounted with a butt similar to an Edison incandescent lamp, and resembles a candelabra lamp. This makes a most convenient method of handling the cell; and by keeping it from the air the disadvantages inherent in all cells heretofore have been very largely done away with.

Another form of Ruhmer cell consists of two fine platinum wires wound on a glass cylinder 1¼ inches long and ¾ of an inch in diameter; the wires which are 1/32 of an inch apart are coated with selenium.

Selenium cells are very susceptible to moisture, and it is largely this taking up of moisture which produces the electrolytic effect in the cell, enabling one to connect it with a galvanometer and produce a current by merely focusing the light upon the cell. This phenomenon gave rise to the designation of the photo-electric cell.

Those who have worked with selenium cells know that heretofore they have been most unreliable; varying their resistances from time to time enormously; and in the case where copper wires are employed, there is a selenide of copper formed, which often renders the cells inoperative in a comparatively short time.

To some extent, the cells made originally have been protected by covering them with mica or lacquer or varnish; but placing them in an exhausted receptacle and mounting them in the manner devised by Mr. Ruhmer is, it seems to the writer, a most important step in the commercial development of the selenium cell.

Prof. Bell has made a number of types of selenium cells, his standard form consisting of alternate disks of brass and mica, with the mica disks slightly smaller than the brass, forming a recess for holding the selenium, which is spread over the surface. All the evenly matched disks are connected to one end of the circuit; and all the old disks to the other end. The cylindrical form of the cell enables it to be acted upon from all directions, when placed lengthwise in the focus of a parabolic reflector. This is also of great advantage in the Ruhmer type of cell.

Selenium cells possess the remarkable property of recovering the original resistances upon the removal of the source of light.

It is well known that in the case of the radiophone, if a beam of sunlight be thus intercepted by a blackened perforated revolving

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disk, a musical note, varying in pitch with the speed of the disk, will be produced in a rubber tube held at the opposite side of the disk. I have here one of the original forms of radiophones.

A piece of apparatus has been devised consisting of a disk with slits near the edge. which is placed near an incandescent lamp, and a selenium cell. If the selenium cell is connected to a telephone and battery, and the disk is rapidly revolved, a musical note will be produced in the telephone, the pitch of which will correspond to the speed of the revolving disk.

Mr. Giltay has recently written me suggesting a very pretty experiment in this line, in which a double vaned Crookes' radiometer is placed between a selenium cell and an arc light shielded by an alum cell. The light from the arc lamp causes the radiometer to revolve intermittently screening the selenium cell and producing a musical note in the telephone attached thereto, the pitch of which is in accordance with the speed of revolution of the radiometer.

I have here to-night two forms of flame telephone transmitters, one of which was presented to me by Mr. Ruhmer, and the other I have purchased from Mr. Giltay, which I have mounted as you see it here and as illustrated in Fig. 20 (about 24 volts are required, depending upon the selenium cell). In each case you will note that I have an acetylene generator which conveys gas to the interior of an otherwise empty telephone transmitter. The diaphragm of these transmitters is made of pig-skin, or a similar material. A tiny pipe runs from the back of the transmitter, and ends in one case to a single acetylene jet, and in the other case to three acetylene jets. By talking against the pig-skin diaphragm, the gas inside is made to vibrate and produces a manometric flame. This flame throws its light upon a selenium cell, to which is connected a battery and a pair of very sensitive telephones between 100 and 200 ohms for each cell of battery, in which the sounds spoken into the transmitter are most perfectly reproduced. A thin sheet of paper inserted between the flame and the selenium cell serves to cut off all sound. It is self-evident that these telephone receivers might be at any distant point. I have worked them over considerable distances.

In Fig. 21 are shown a number of most interesting applications of the selenium cell in conjunction with a battery and relay, used for starting a motor, ringing a bell, firing a cannon, blowing a horn, and lighting incandescent lamps, all of which experiments

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I shall hope to show you in actual operation, as I have had them working most successfully in my laboratory; and you will see that by merely passing my hand before the selenium cell, I can start and stop the motor, turn the light on and off, and ring the bell and blow the horn, or I can fire this cannon, start my phonograph talking, etc. I am indebted to the courtesy of the Marconi Co. for the large relay used in certain of these experiments.

I have here also a 3 h.p. motor, driving a 1½ k.w. generator and

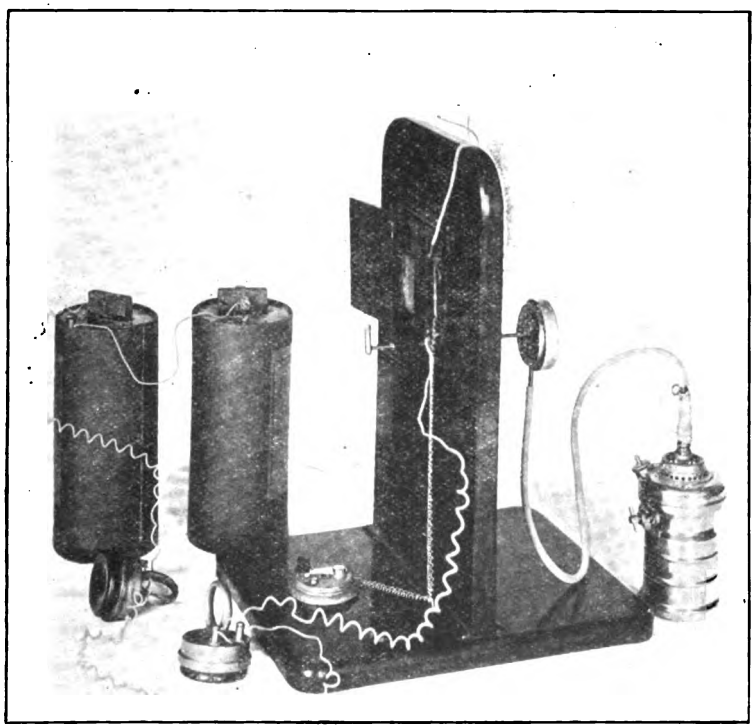

FIG. 20.—Manometric Acetylene Flame Transmitter with Selenium Cell, etc. —(a battery of about 24 volts employed.)

supplying these lamps which have been courteously supplied by the General Electric Co.; and by means of this selenium cell, relay, battery and a motor starter, for which I am indebted to the Cutler-Hammer Co., I hope to be enabled to start and stop the motor by merely passing my hand before the selenium cell.

In Figure 22 is shown a portion of the stage setting at the

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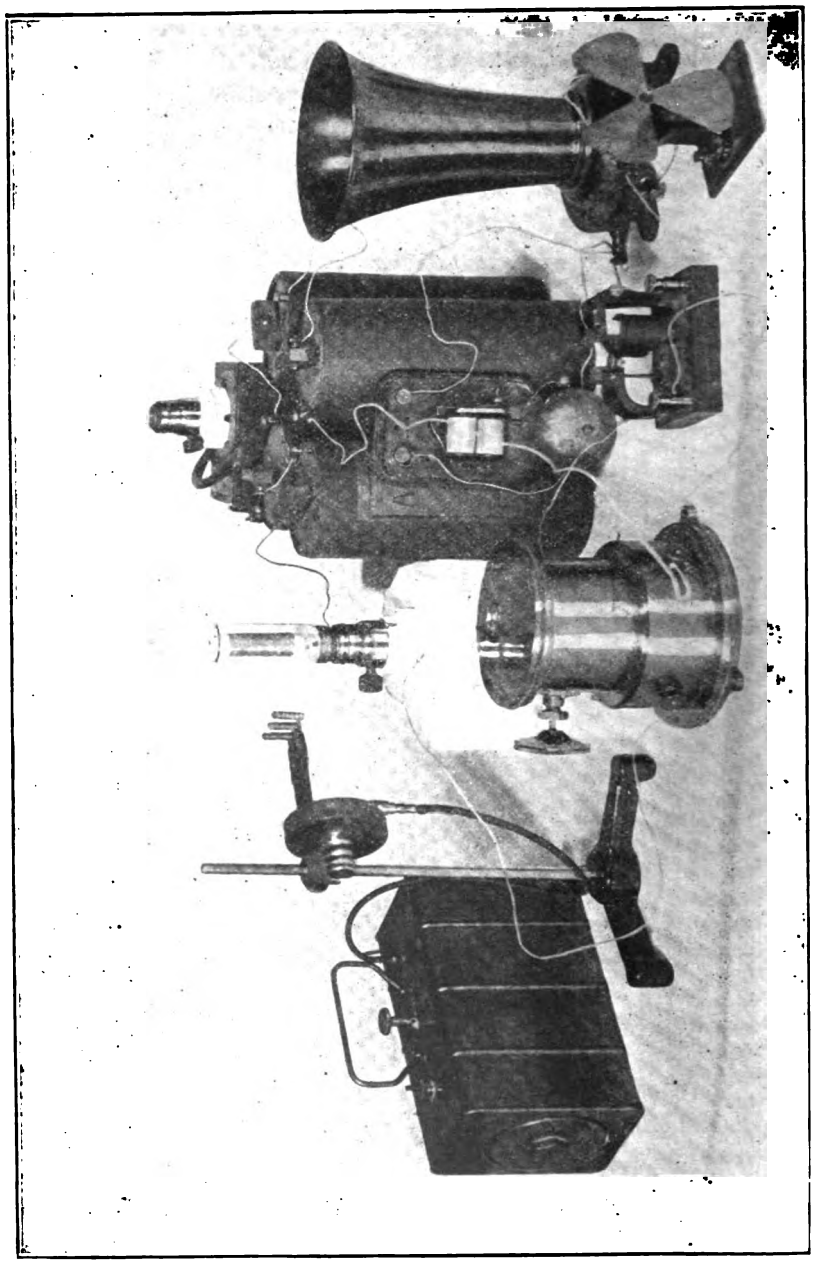

FIG. 21.—Acetylene Flame Apparatus, Ruhmer Selenium Cell, Relays and Battery for Operating Electric Lamp, Bell, Motor and Horn. (A 3 H.P. Motor and Generator were also similarly operated and a cannon fired.)

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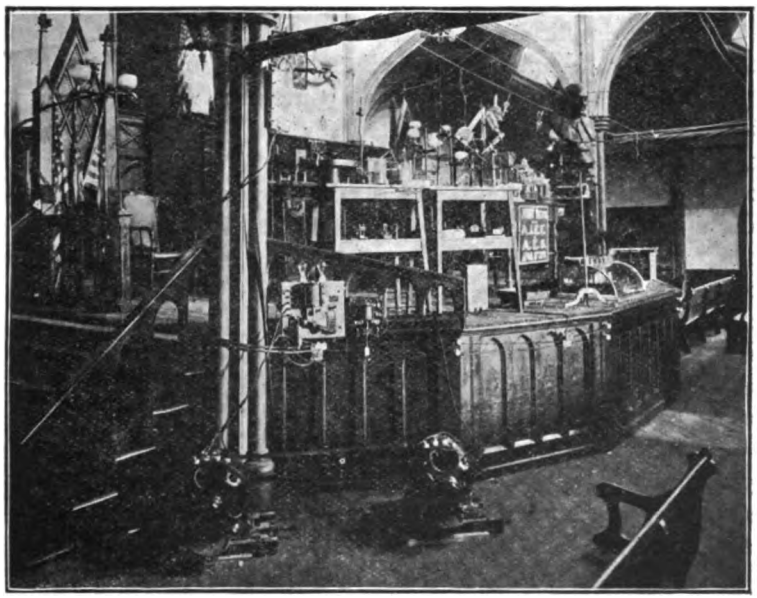
lecture, and shows in the foreground the three horse-power motor and generator which supplied a bank of lamps, and which plant was started and stopped many times when the author passed his hand between the acetylene flame and a selenium cell. The frontispiece is a general view of the stage setting in the College of the City of New York, and was taken shortly before Mr. Hammer's lecture.

In 1886 the writer attended a convention of the Edison Association of Illuminating Companies at Rochester, New York, and



IG. 22.—Three H. P. Motor and Generator supplying Bank of Lamps and operated by shielding with the hand a Selenium cell from an Acetylene Flame.

during a discussion of contract systems versus meter systems, he gave his experience as chief inspector of central stations of the Edison Company, in dealing with the difficulties met with in supplying light by contract; and he then described a practicable method of utilizing selenium cells to control relays and magnets which would throw off the electric lights on the approach of day and on again at night, thus solving the difficulty of street lighting, and other circuits intended to operate only at night.

On February 12, 1890, in a paper on some experiments with

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selenium cells, Mr. Shelford Bidwell showed a relay operated by a selenium cell, which threw on an electric lamp and rang a bell; and he suggested the protection of safes and strong rooms by selenium cells, which would be affected by the light from a burglar's lantern, thus giving an alarm. He also spoke of their being used to give notice of the extinction of railway signal lamps and ship lights, and stated the following: "But I do not at present attach any serious importance to such practical applications of these devices. I regard them simply as offering somewhat attractive illustrations of the effect of light upon the resistance of selenium."

This is an important statement from the greatest authority on the subject of selenium, but to-day it will not hold good.

I hold in my hand a small vial containing some "thermit," which was discovered by Dr. Goldschmidt. It consists of oxide of iron, such as one would get off of a blacksmith's anvil, or from the rolls of a rolling mill, and is mixed with powdered metallic aluminum. A red hot iron or molten cast iron poured into this mixture produces no effect; but if a little barium preparation or magnesium powder be placed on top of this mixture and touched off by a match, an extraordinary reaction takes place, producing a temperature of about 3000° C., and the mechanical equivalent of a kilo (2.2 lbs.) of thermit is about 1,730 horsepower seconds or 1,273 kilowatt seconds.

I have seen some very interesting experiments made in welding girder rails, pipes, etc., by this process, and have here some interesting samples of manganese, chromium, ferro-titanium and other metals prepared in this way.

I have also seen steel safes in which enormous holes had been burned by employing thermit; and it would be possible for a burglar to carry some thermit in his pocket and burn a hole in a safe large enough to insert his arm and extract the valuables.

I also saw in Germany last summer a substance called "anti-thermit," which it is intended to place in the lining of safes to prevent the reaction taking place, thus protecting the safe. But a simple plan would be to place a selenium cell in or near the safe, so that the moment the reaction was started, a signal would be given to the police in a similar manner, as suggested by Mr. Bidwell in the case of the burglar's bull's-eye lantern.

An important commercial application of the selenium cell has recently been made by Mr. Ernest Ruhmer in connection with his electrically controlled buoy illustrated in Fig. 23.

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Pintsch has constructed a large number of buoys containing compressed gas, which would last from one month to upwards of a year; but it was heretofore necessary to burn these lights day and night, it being often impracticable by reason of distance at which they were placed, and frequency of storms, etc., to switch off the gas so that it would not burn during the day time.

Mr. Ruhmer has placed one of his selenium cells in the top of such a buoy connected with a switching device which, as soon as the sun rises in the morning, causes the selenium cell to reduce its resistance, this causing the switching device to turn off the gas, which is again turned on upon the

FIG. 23.—Pintsch Gas Buoy Controlled by a Ruhmer Selenium Cell, Battery and Switch Mechanism.

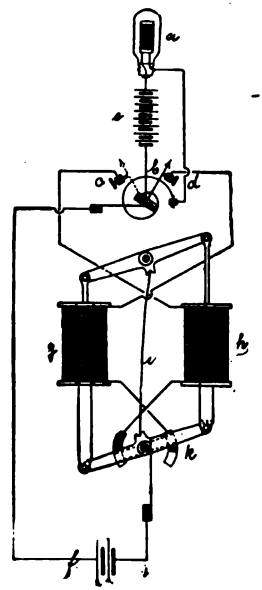

FIG. 24.—Diagram of Circuits of "Selenium" Buoy.

increase of resistance of the selenium cell by the approach of night-fall, or if desired in the case of a storm coming up. A buoy containing sufficient gas for one month could thus be made to answer without recharge for from three to five months.

The arrangements of the circuits as originally devised by Mr. Ruhmer is shown in Fig. 24. The voltmeter needle has been replaced by a relay, and the apparatus simplified. A single dry cell is interpolated in the selenium cell circuit, as usually employed on the buoy; and this cell will last a year or more; and with the relay, it is placed in the bottom of the buoy and arranged to be absolutely waterproof.

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When I was in Berlin last August, one of these buoys had been in operation since the previous October, turning the light on and off every night and morning; and Mr. Ruhmer has recently written me that it is still operating successfully, as are others which he has placed near Hamburg and in the Baltic Sea.

Mr. Ruhmer has also constructed an apparatus employing the selenium cell to which he has given the name "photographophone," which is one of the most remarkable pieces of scientific apparatus that it has ever been my pleasure to see. Figs. 25, 26

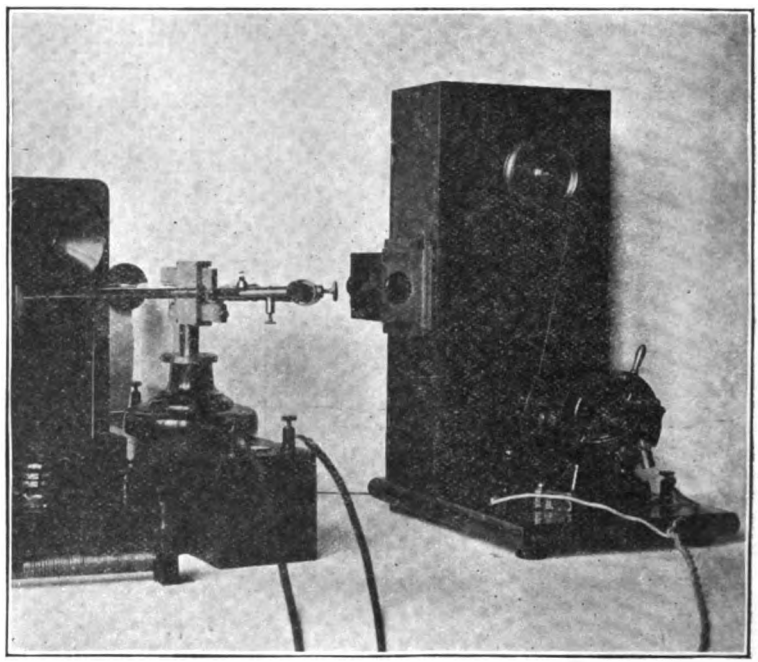

FIG. 25.—Ernest Ruhmer's Photographophone, Showing Exterior View, together with Telephone Transmitter and Arc Lamp.

and 27 illustrate the general construction of the apparatus, which I shall further illustrate by accompanying lantern slides. In Fig. 28 the apparatus is shown diagramatically and in Fig. 27 the inventor is shown listening to the photographophone reproducing speech and music. It consists of a box containing a gelatine or celluloid film, such as employed in moving picture machines, which is driven at high speed by means of an electric motor. In the front face of the box is set a cylindrical lens about the size of one's little finger. A short

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distance away from the box is placed an arc lamp and a telephone. Words spoken or sung into the telephone superimpose the waves in the telephone circuit upon the current flowing in the arc light circuit, and cause a corresponding variation in the light of the arc. The rays from the arc lamp pass through the cylindrical lens already referred to, and are caused to fall in sharp white lines on the moving sensitive film. This film, upon being taken out of the box and developed, shows a series of perpendicular striations parallel to one another, which are really a photographic record of the sound waves originally entering the telephone transmitter. Where the striations are fine and close together, the pitch is high, but where they are broader and farther apart the pitch is low. Strips of the films or photograms are shown in Fig. 29. The developed film is next placed back into the box and the motor again started. The arc lamp remains in its original position, but

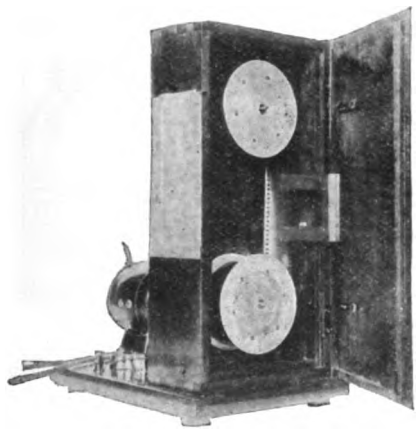

FIG. 26.—Showing Interior of Ruhmer's Photographophone.

burns steadily as the telephone is not operated. The rays from the arc lamp passing through the lens are therefore quite uniform, and the moving gelatine strip acts as a screen to cut off these rays, allowing the light intermittently to fall upon the selenium cell at the back of the box, producing a variation in its resistance and a corresponding effect in the telephone receivers connected thereto. A battery is also interpolated in the circuit with the selenium cells and the telephones. By holding these telephones to the ear, the reproduction of the sound is perfect, as I can vouch for from personal experience with the apparatus.

Mr. Ruhmer contemplates utilizing this photographophone as a receiving instrument with its wireless telephone system, in which he employs a beam of light, as already described.

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Mr. Shelford Bidwell has also made a device for producing pictures or writing at a distance by combining the properties of selenium with the chemical telegraph.

Various inventors have endeavored to solve the problem of seeing what goes on at a distance by employing selenuim. Among these are Perosino, Senlecq, de Paioa, Cary, Sawyer. Larroque, Nipkow, Gemmill, Liesegang, Heinzerling, Edison, Stern, Jan Szczepanik, Dussaud, Otto von Bronk, von St. Schneider, Ayrton and Perry, Korn, and others, who have proposed various methods employing images thrown on ground glass or through a photograph negative, or upon mirrors swinging synchronously, by or

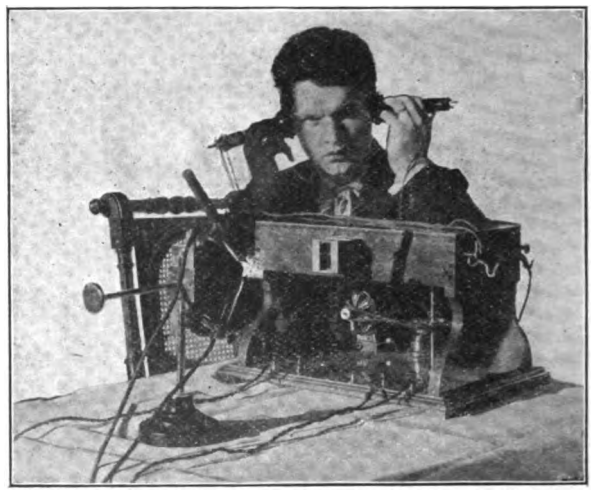

FIG. 27.—Mr Ernest Ruhmer Listening to his Photographophone.

using revolving perforated screens, for cutting off the beams of light, multiple selenium cells which would be affected by high lights and low lights of the original picture, etc., these devices affecting some method of illumination at the receiving end or producing an electrochemical action such as is produced by the usual chemical telegraph systems, or controlling an electropantograph system such as Gray's telautograph. These various inventions have been termed the telescope, telephote, telectroscope and the telephotograph. But these devices have thus far reached little further than descriptive matter, drawings and crude experiments.

Various people have suggested the use of selenium cells for photometric purposes; and it is interesting to note that Mr.

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Latimer Clark suggested this application the evening in which Mr. Willoughby-Smith first brought to public notice the phenomena of variation in resistance of selenium when exposed to light, to which I have already referred.

Mr. Fritts has suggested making a form of photomoter which would be sensitive to lights of different color, as well as of varying candle power, by employing as a film on the surface of his cell a gold foil which transmits green rays, a silver foil the blue rays, and so on; and suggests that a solid transparent conducting film which would transmit all of the rays would be far better and thus remove the color stumbling block in photometric work.

Sir William Crookes has constructed an exceedingly interesting type of radiometer, in which he has coated the revolving vanes on one side with selenium, and on the other with chromic acid. He

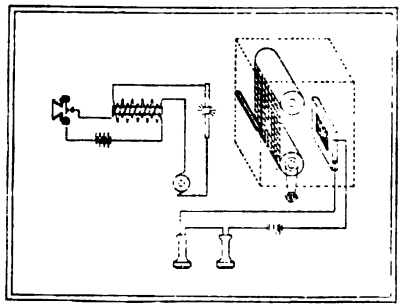

FIG. 28.--Showing General Arrangement of Circuits of Ruhmer's Photographophone.

found that the white light from a sperm candle repelled the selenium, while the yellower light of the wax candle repelled the chrome, thus indicating the relative absorptive powers of the different substances for rays of different refrangibility, resulting in mechanical motion; just as the same selective capacity operates in photography as chemical action.

In 1891 Prof. Barnard of Lick Observatory employed a selenium cell as a device for automatically detecting comets, and Minchin has employed the selenium cell quite extensively in his astronomical investigations.

In Fig. 30 is shown a curve which Mr. Ruhmer recently sent me which shows some observations made by means of his selenium cell during an eclipse, these being the only observations which anyone was enabled to make at that time, on account of stormy weather. Mr. Ruhmer has prepared an interesting paper bearing on this and other applications of the selenium cell to meteorology. He made his observations on October 31, 1902.

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Selenium is found in Vesuvian lava, and in natural sulphur as a sulphur selenide in the Lispari Islands. It is also found in Norway and other iron pyrites. It occurs in meteoric iron and in such rare metals as eucarite as a selenide of silver and copper in Sweden and Chili; crooksite, a selenide of copper and thallium with a little silver, from Norway; as clausthalite, a selenide of lead in the Hartz Mountains, from Zinken and Clausthal, in Inverg, Rheinberg, Saxony, Rio Tinto, Spain, Mendoza, South America; as riolite at Culebras, Mexico; as Lehrbachite, a

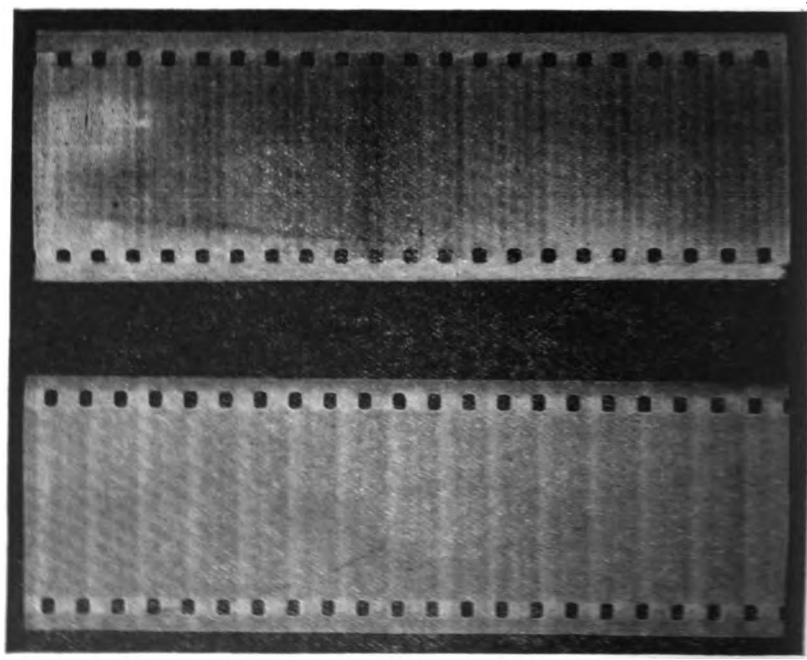

FIG. 29.—Photogram as used in Ruhmer's Photographophone (High Pitch Tones above, Low Pitch below).

selenide of mercury and lead from the Hartz Mountains; as zorgite, a selenide of copper and lead from Glasbach in the Hartz Mountains. Selenium, although widely distributed over the globe, occurs only in small quantities and in some instances is found in native state.

Selenium is placed among the rare metals. Chemically pure crystalline selenium costs about $1.00 per gramme; and the ordinary commercial article about 10 cents per gramme.

The Bibliography of selenium is quite extensive. Those interested in the subject will find an excellent paper by Mr. A. P. Saunders

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in the *Jour of Chem.* for June, 1900. The paper contains many references, and is entitled "Allotropic Forms of Selenium."

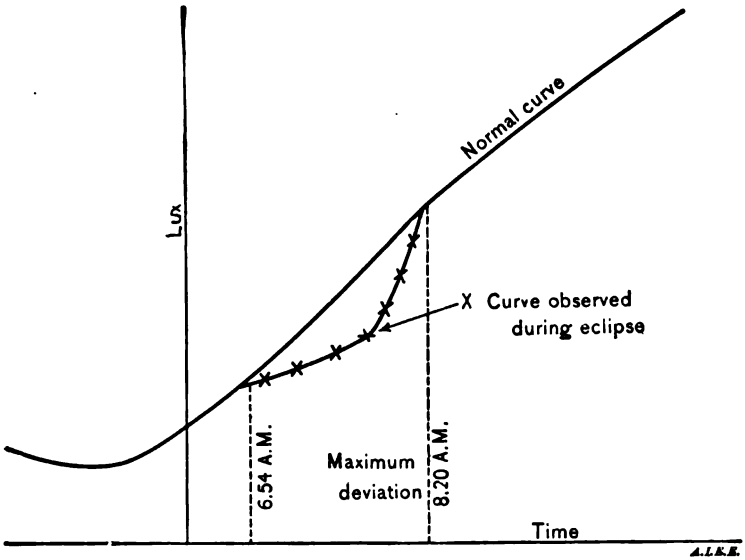

FIG. 30.—Curve Taken with Ruhmer Cell During Eclipse, Oct. 31, 1902

THE TREATMENT OF DISEASE BY ULTRA-VIOLET RAYS

PROF. NIELS R. FINSEN.

Some professional matters detained the writer in Copenhagen last summer for several weeks, and during his stay in that city he had the privilege of visiting the Finsen Light Institute at Rosenvaengat, a suburb of Copenhagen, and was enabled to investigate the system for the treatment of disease by light, inaugurated by Dr. Niels R. Finsen. In Figs. 31 and 32, are shown views of the operating room at the Finsen Institute, where a large number of patients from various parts of Europe were undergoing treatment at the time of my visit.

Dr. Finsen has conducted very extensive and most painstaking

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researches into the bacteriacidal effects of light, and he has found the violet end of the spectrum to possess remarkable curative powers, and he has also found that by utilizing the blue, violet and ultra-violet rays of the spectrum, those loathsome diseases of tuberculosis of the skin and lupus, diseases which have baffled surgical skill heretofore, have been successfully combatted.

It has recently been stated that in New York City alone there are annually 20,000 cases of tuberculosis, with 8,000 deaths; and there is probably no disease with which mankind is afflicted which compares in deadly character to tuberculosis.

In affecting certain of the internal organs, it is known as consumption, and appearing externally, attacking the skin and underlying tissues, it is known as lupus vulgaris. As a rule, it appears in single patches, most frequently attacking the face, especially the nose, cheek and mouth. It may, however, attack the extremities or, in fact, any portion of the body and even mucus membranes. Fortunately, lupus is rather rare in this country, although very common in Europe.

Koch and others have fully demonstrated that tuberculosis is due to the presence of specific organisms named "tubercle bacillus," which have been found to be present in both the internal and cutaneous forms of the disease.

Doubtless many present remember the "blue glass craze," which swept over the country in 1876, or thereabouts.

I have with me here a copy of General A. J. Pleasonton's book entitled, "Blue and Sunlights, Their Influence upon Life and Disease," which I picked up in a second-hand book store some years ago; and I would commend the examination of this book to all who are interested in the subject. General Pleasonton and his system were condemned to both abuse and ridicule. Dr. Finsen, however, says, "The General was absolutely on the right track."

For a considerable time Finsen's work received little credence and no encouragement; but he persisted in his investigations, and the results secured by him finally bore fruit, and to-day the world rings with his praises. In all parts of the civilized world his work is being taken up, and institutes are being founded for the treatment of disease by light rays—particularly the ultra-violet light. In England the initiative was taken by Queen Alexandra, and in Russia by her sister, the Czarina, they both investigating the system while visiting their father, the King of

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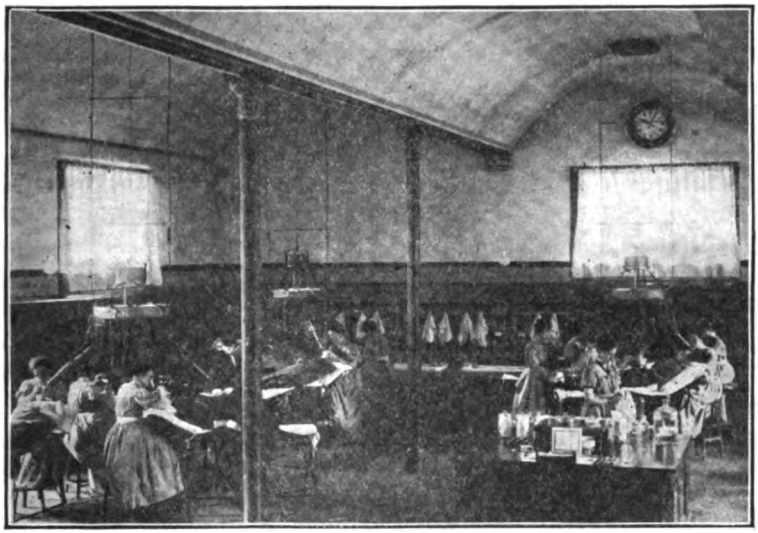

FIG. 31.—Showing Main Operating Room, Finsen Institute, Copenhagen.

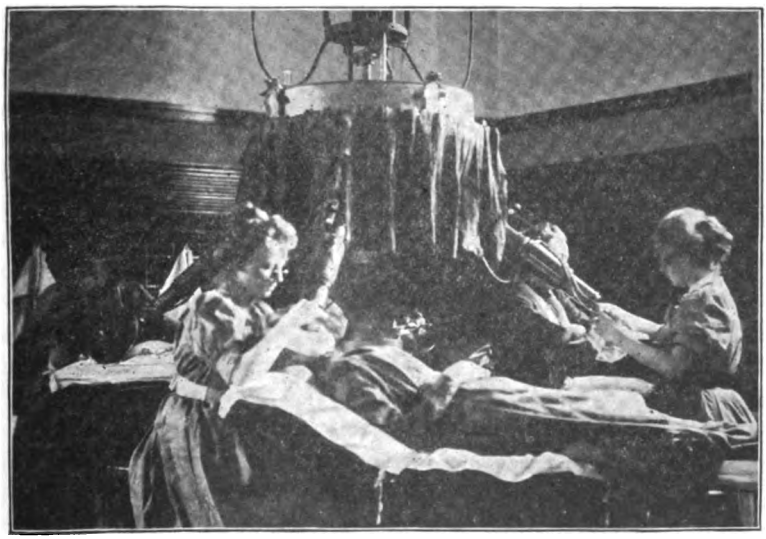

FIG. 32.—Showing Arc Lamp and Four FinsenTubes in Use at One Time.

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Denmark. Much has also already been done in the United States.

It will be remembered that during Queen Elizabeth's reign a certain court physician recommended strongly that patients suffering from small-pox should be kept in a room, the decorations of which, including the hangings, bed draperies, etc., should be red in color, claiming that the red light had a soothing effect upon the irritated portions of the skin, lessening the severity of the disease. Little importance was attached to this method, and the originator of it was branded as a Charlatan.

Prof. Finsen, has, however, found that this method of treatment of small-pox is of paramount importance. He has placed patients in a room into which the sun's rays could only penetrate through sheets of red glass, just as they would penetrate a photographic dark room; and he has found that patients placed in such a room prior to the most painful and most dangerous suppuration stage setting in, that suppuration has been entirely prevented and that the scarring has been in nearly all cases absolutely prevented, and in the few cases where there was any scarring, it was hardly perceptible. The disease has been in a much milder form, the fever usually accompanying the eruption disappearing, and the temperature remaining normal.*

He has found that the use of ultra-violet light on these patients very much aggravated the disease, and even in cases where patients were almost cured and they have been allowed to go out into the sunlight, the disease has at once been aggravated.

In connection with his investigations into the effects of light Finsen made some interesting and ingenious experiments upon earth-worms placed in a box, one-half of which was covered with red glass and the other half blue glass; and he found the blue light irritated the worms so they invariably crawled under the red glass, and a chameleon, placed with its body midway between the glasses, turned almost jet black under the influence of the blue rays, while that portion under the red glass remained nearly white, which Prof. Finsen says showed that the chameleon was altering its pigment cells to lessen the irritating effects of the blue light.

The ultra-violet end of the spectrum contains the most refrangible rays, and it is these rays which are so harmful in cases of smallpox; and it is also these actinic rays which produce sun-

* Prof. Finsen has recently written the author that placing the patients in a dark room is fully as efficacious as placing them in a room lighted with red rays only, the important thing being to keep the patient from exposure to the actinic rays

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burning, which one often experiences in the Alps, or any high altitude where the temperature may be considerably below zero; and there are doubtless many present who have experienced considerable effect similar to sunburning by working in close proximity to arc lamps.

While these ultra-violet rays are so harmful in the case of smallpox, they are of the precise nature which is most desirable in the treatment of such diseases as tuberculosis of the skin or lupus vulgaris. These rays not only destroy the bacilli, but they excite and stimulate nutrition and excite activity in granulation, thus assisting very greatly in the rapid recovery from the disease.

Doubtless the rays emanating from the sun are very rich in blue, violet and ultra-violet light; but the atmosphere readily absorbs these rays, and while Prof. Finsen for a time used the sun's rays in the treatment of tuberculosis of the skin and lupus he found that by employing the arc light the same effect could be produced in a very much shorter space of time; and that he was in this way, also, independent of weather conditions.

The arc light is much richer in ultra-violet rays than the sunlight; and Broca and Chatin of Paris have found that by placing an iron core inside of the positive carbon electrode, this arc was still richer in ultra-violet light, and Görl of Erlangen, has constructed a form of aluminum arc, in which four arcs were formed between five aluminum electrodes. I have here a modification of Görl's lamps constructed by Messrs. Waite & Bartlett of this city, in which there are four iron electrodes forming three iron arcs in series, which produce an intense source of ultra-violet light. which I shall presently show in operation.

Bang and others have also made arc lamps employing terminals of iron.

It is claimed that by employing the iron arc the same results which take an hour and ten minutes by means of the carbon arc can be accomplished in twenty minutes to half an hour; and also that so intense are these ultra-violet rays it is not necessary to use pressure to drive the blood away from the diseased part, and it is also unnecessary to use water to cool the rays.*

Drs. Piffard and Jamieson have suggested the use of suprarenal extract in the form of adrenalin chloride, which the former prefers to introduce into the skin around the diseased spot

* Prof. Finsen has recently written the author emphatically asserting that iron electrodes are not as efficacious as carbon electrodes as the rays from the iron arc, he claims, do not penetrate as deeply as the rays from the carbon arc.

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by cataphorisis, thus producing a whitened area from which the blood has been withdrawn, which enables the treatment of this portion by the ultra-violet light, without pressure being applied, and the blood does not return for half an hour or more. The cataphoric electrode is covered with a thickness of lentine saturated with adrenalin connected with a positive pole of the battery, using a current of from three to four milli-amperes, the bleaching taking from four to five minutes' time.

The Roentgen rays have been found very effective in the treatment of certain diseases, especially where hard tubes are employed, and as we are considering particularly the treatment of lupus vulgaris, I would call attention to Fig. 33, which repre-

FIG. 33.—Lupus Vulgaris Cured by X-rays.

sents a patient treated by my friend, Dr. William H. King of this city, in which the X-Rays successfully cured a case of lupus vulgaris brought on by the patient's pricking a tiny boil on the side of his nose with a pin taken from the lapel of the coat of a friend who was suffering from tuberculosis (consumption). The rapid progress of the disease is shown in the illustration and was taken three weeks after using the pin, and was largely augmented by the man's age (45), and his being in poor health (a chronic rheumatic). Two bacterialogical examinations showed conclusive evidence of the presence of tubercle bacilli.

In Fig. 34 is shown the original blue lens used by Finsen when employing sunlight. It consists of a flask full of light blue ammoniacal sulphate of copper. The bottle with its contents

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makes a plano-convex lens. The sunlight passing through this is found to work very well; but it was too slow, and the sun was frequently obscured. Finsen later used plain water, finding that the blue water cut off most of the ultra-violet rays and he found the clear water very largely absorbed the ultra-red rays which caused the heat.

In Fig. 35 is shown a form of telescope which is now adapted in standard practice at the Finsen Institute. It contains four rock crystal lenses, which act to cut off considerable of the heat rays but allows the ultra-violet light to pass through it.

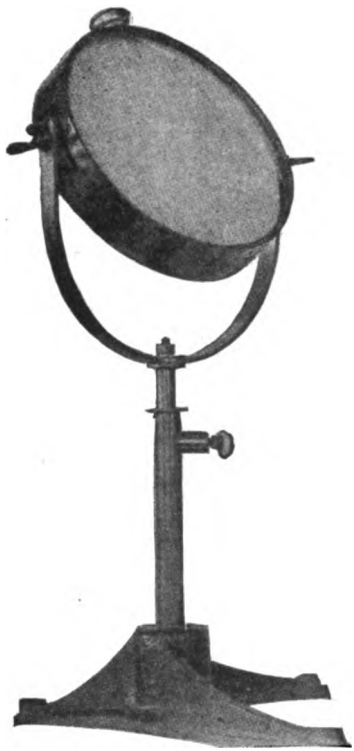

FIG. 34.—Finsen's Original Blue Lens for Use with Sunlight.

It will be remembered that ordinary glass cuts off almost all of the ultra-violet rays, whereas a block of rock crystal 4.4 mm. thick will allow 60 per cent. of the ultra-violet to pass through it.

A part of the heat is also absorbed by the distilled water which is contained inside of the telescope. In order to keep this water cool, there is an outside jacket on the telescope, through which circulating water may be passed for this purpose. In Fig. 36 is shown the method of arrangement of the telescope and the arc lamp; and in Fig. 32 is shown a set of four of these telescopes arranged around the arc lamp and in actual operation. The arc lamp uses from 40 to 80 amperes and operates at 45 to 50 volts.

Blood is opaque to ultra-violet light, and it is therefore necessary to drive the blood away from the diseased portion which is to be treated. This is accomplished by what is known as a pressure glass shown in Fig. 37. It consists of a plano-convex lens of rock crystal kept cool by circulating water—the glass acting to focus the light on the diseased portion, and also to exert considerable pressure there.

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The patient does not suffer from exposure to the rays; but after the treatment, which is usually an hour and ten minutes per day, he appears to be considerably sunburned. He is then allowed to recuperate until the next day, and the treatment is then repeated. After a series of these treatments, the patient is sent away apparently cured. Sometimes he does not return; but more often he must come back for a second or third, and even more series of treatments, due to the fact that certain of the

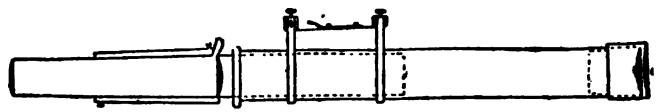

FIG. 35.—Finsen Telescope Tube, for Use with Carbon Arc Light.

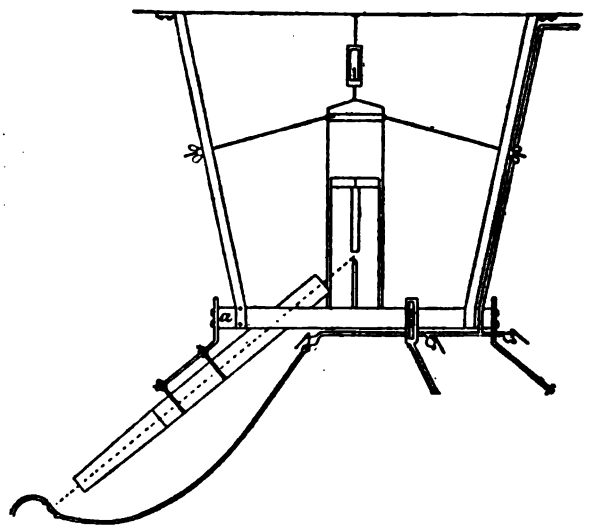

FIG. 36.—Showing Arrangement of Arc Lamp and Finsen Tubes.

microbes which have been deep-seated have worked their way to the surface, the disease having started anew.

It is said that out of over 600 cases treated at Copenhagen, there have been only 1 to 2% of failures due to fault in the treatment; but there have been cases where the disease has been in such an advanced stage and for such a very long period that it has not yielded successfully. But I was informed that in the majority of cases after very few treatments, the patients are dismissed absolutely cured. In order that you may properly

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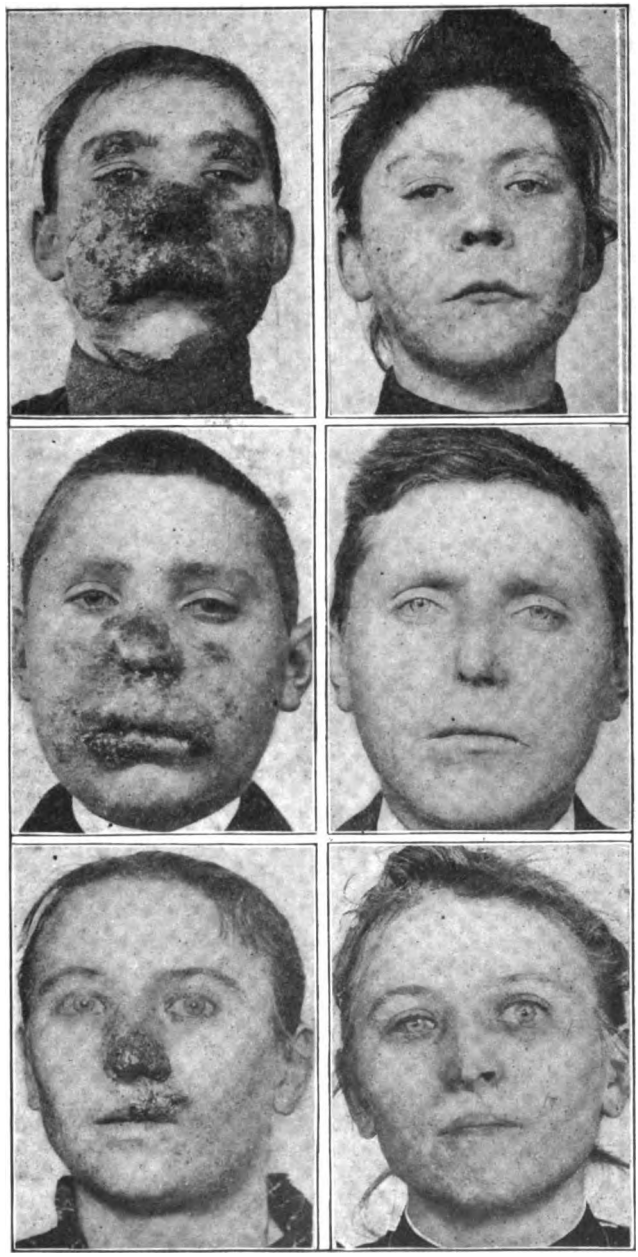

FIG. 38.—Showing Lupus Vulgaris Patients Before and After Treatment with Ultra Violet Light at the Finsen Institute, Copenhagen.

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appreciate the remarkable results which have been secured by Prof. Finsen; and the stupendous importance which his successful combatting of these loathsome forms of disease represents to many of the most sorely afflicted people of this world, I have inserted in my paper several photographs, see Fig. 38, which I secured at the Finsen Institute; of patients afflicted with lupus vulgaris—these pictures showing them before and after the treatment with the ultra-violet rays produced by the arc light I feel that their presentation in this paper requires no apology, on the contrary, electrical engineers should feel a sense of pride that in the use of the arc light in this remarkable advance in medicine and surgery, their profession has contributed in no small degree.

Those caring to look up these and similar cases, will find full descriptions in English in " Phototherapy after Finsen's Methods," by Valdemar Bie, M.D., Prof. Finsen's Assistant (published

FIG. 37.—Pressure Lens.

by Lippincott), or Die Bekampfung des Lupus Vulgaris von Niels R. Finsen (Gustav Fischer Jena), and Die Finsen Therapie und ihr gegenwartigen stand in des Dermatolo-gie, von Dr. Forchhammer 1. Cohen's Buchdruckereien Kopenhagen).

The little cut of Prof. Finsen which heads this article is from an autograph portrait which Prof. Finsen presented to the writer, and it is sad to contemplate that this man who has conferred such a priceless boon upon humanity is himself an invalid, suffering from an incurable disease, and one which has made it at times well nigh impossible for him to prosecute his work.

The Finsen Institute was established in 1896, through the munificence of Copenhagen's public-spirited citizens, and through a gift by the city of the property on which it was erected.

The lecturer desires to express his appreciation of the services rendered by his assistants, Messrs. Varley, Lawton, Brown, Webb, Scheerer and Dow, and also to acknowledge the courtesies extended by the New York Edison Co.

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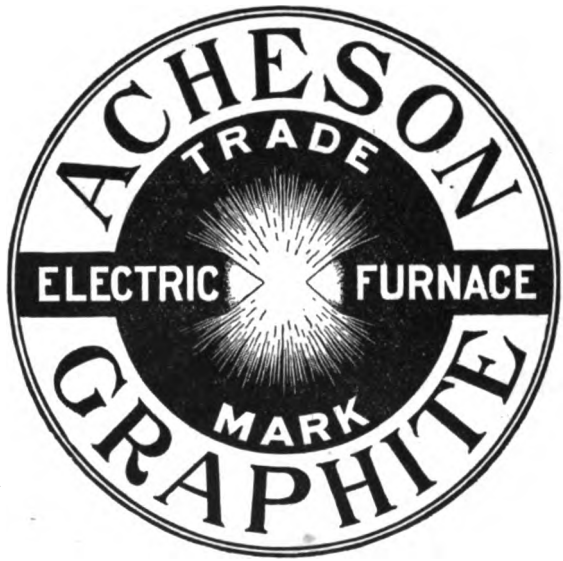

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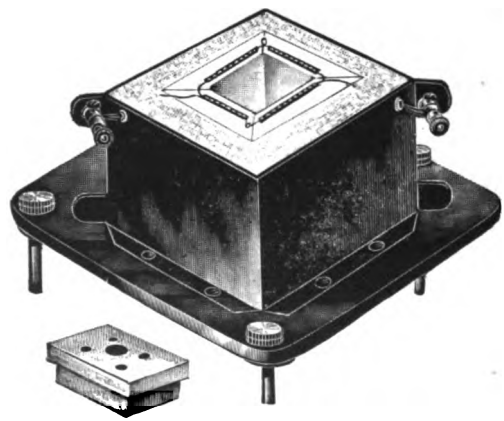

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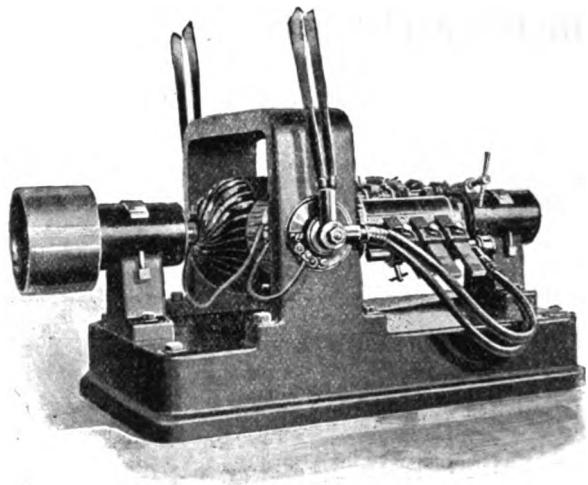

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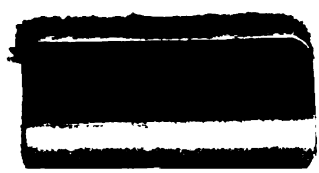

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